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## PERFLUORINATED AROMATIC COMPOUNDS

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## FOREWORD

This report, "Perfluorinated Aromatic Compounds" for the period 1st December, 1963 to 30th November, 1964 covers work under Contract No. AF 33(615)-1344. The work was performed by Monsanto Chemicals Limited, Ruabon, Great Britain, and by Imperial Smelting Corporation (N.S.C.) Limited, Great Britain, under subcontract from Monsanto Research Corporation.

Part I of the report describes the work done by Imperial Smelting Corporation on fluoroaromatic intermediates. Part II describes the work done by Monsanto Chemical Limited on model compounds and polymers.

The work is administered by the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. Lt. D. G. Holland is project engineer. For Monsanto Research Corporation, Dr. J. M. Butler serves as contract coordinator. For Monsanto Chemicals Limited, Dr. E. B. McCall serves as project leader, assisted by W. Cummings and E. R. Lynch; R. A. Lidgett is responsible for infra-red and gas chromatographic examinations. For Imperial Smelting Corporation Limited, Dr. A. K. Barbour serves as project leader, assisted by M. W. Buxton, J. Tilney-Bassett and R. Mobbs.

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This technical report has been reviewed and is approved.

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## ABSTRACT

Preparations or synthetic studies have been carried out on tetrafluoroisophthalic acid, difluoropyromellitic acid, the tetrafluorophenylene diamines, decafluorodiphenylamine, 3,3',-4,4'-tetra substituted-hexafluorobiphenyls, tetrafluororesorcinol, perfluoroaromatic thio-ethers, and dithiols. These and other perfluorinated aromatic compounds are the intermediates employed in the synthesis of perfluorinated model compounds and polymers. The thermal stabilities of such compounds and polymers have been compared with the thermal stabilities of their hydrogenic analogues. Structures investigated include amides, imides, esters, carbonates, oxadiazoles, triazoles and sulphides.

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P A R T      I.

## A. INTRODUCTION

The objective of Imperial Smelting Corporation's part in this programme is the provision of samples of perfluoroaromatic intermediates required by Monsanto Chemicals Limited for synthesis of model condensates and polymers which are used for thermal stability tests.

The work described is a continuation of the programme carried out in the period 15th April, 1963 to 30th November, 1963 which was reported in Technical Documentary Report No. ML-TDR 64-89. It has been mainly concerned with devising preparative methods for tetrafluoroisophthalic acid, difluoropyromellitic acid, tetrafluorophenylenediamines, decafluorodiphenylamine, 3,3',4,4'-tetrasubstituted-hexafluorobiphenyls, tetrafluoro-resorcinol, perfluoroaromatic thioethers and dithiols.

## B. SUMMARY

A small quantity of tetrafluoroisophthalic acid was prepared by metalation and carbonation of 1,2,3,5-tetrafluorobenzene and by hydrolysis of decafluoro-m-xylene. Two other syntheses are under investigation.

Difluoropyromellitic acid has been obtained by a six-stage synthesis from durene.

Tetrafluoro-m-phenylenediamine of about 90% purity was obtained by heating pentafluoroaniline with ammonium hydroxide; the major impurity appears to be the para-isomer. A preliminary investigation is being made of a route to the meta diamine involving nitration of 1,2,3,5-tetrafluorobenzene. Tetrafluoro-p-phenylenediamine was prepared from pentafluorobenzonitrile in 10% overall yield. Tetrafluoro-o-phenylenediamine was prepared in 11% overall yield by a six-stage synthesis from 1,2,3,4-tetrafluorobenzene.

Syntheses of 3,4,3',4'-tetraminohexafluorobiphenyl and 3,3'-dihydroxy-4,4'-diaminohexafluorobiphenyl have been achieved, starting from 4,4'-diamino-octafluorobiphenyl.

A satisfactory synthesis of decafluorodiphenylamine has been devised in which the sodio-derivative of pentafluoroaniline reacts with hexafluorobenzene.



Tetrafluororesorcinol was prepared in 47% yield by heating pentafluorophenol with an aqueous solution of potassium hydroxide.

1,4-Bis(pentafluorophenylthio)tetrafluorobenzene, 1,3-bis(pentafluorophenylthio)tetrafluorobenzene and 4,4'-bis(pentafluorophenylthio)octafluorobiphenyl were prepared by reactions of cuprous pentafluorothiophenate with the appropriate perfluoro-aryl dibromide.

Studies have started of routes to perfluoro-aromatic thiols involving dealkylation of thioethers.

The following fluorinated aromatic compounds were supplied to Monsanto Chemicals Limited, Ruabon, and to U.S.A.F., Dayton, Ohio:-

M.C.L. Ruabon

	<u>g.</u>
Tetrafluoro-m-phenylenediamine	32
Tetrafluoroisophthalic acid	51
4,4'-Dihydro-octafluorobiphenyl	20
Pentafluorophenol	100
Pentafluorobenzaldehyde	20
Tetrafluorohydroquinone	15
Tetrafluororesorcinol	25
3,4,3',4'-Tetraminohexafluorobiphenyl	20
Pentafluorobenzoic acid	165
Decafluorodiphenylamine	25
Pentafluorobenzonitrile	50
1,4-Bis(pentafluorophenylthio)tetrafluoro- benzene	4
Tetrafluoro-p-phenylenediamine	4.5
1,3-Bis(pentafluorophenylthio)tetrafluoro- benzene	2.5
Tetrafluoro-o-phenylenediamine	0.5
4,4'-Bis(pentafluorophenylthio)octafluoro- biphenyl	2.5
Pentafluoroaniline	25
Tetrafluorophthalic acid	20
3,3'(?)-Dihydroxy-4,4'-diaminohexafluoro- biphenyl	19.5

U.S.A.F., Dayton

Octafluoronaphthalene	250
Tetrafluoroterephthalonitrile	100
2,3,5,6-Tetrafluorothiophenol	100
1,3-Dibromotetrafluorobenzene	100

## C. DISCUSSION

### 1. TETRAFLUOROISOPHTHALIC ACID (I)

Our unsuccessful attempts to convert either 1,3-dibromo- or 1,3-diiodotetrafluorobenzene into tetrafluoroisophthalonitrile by reaction with cuprous cyanide in dimethylformamide were described in a previous Report (ref. 1). Also in that Report is described the metalation and carbonation of 1,2,3,5-tetrafluorobenzene which gave, in a small-scale experiment, a 12% yield of I. This reaction has now been carried out on a larger scale but a lower yield (8%) of I was obtained; also isolated was 2,3,4,6-tetrafluorobenzoic acid (4%), presumably arising from incomplete carbonation.

Attempts to prepare I by carbonation of 1,3-dilithiotetrafluorobenzene derived from butyl lithium and 1,3-dibromotetrafluorobenzene (ref. 2) gave, in our hands, a brown, resinous, intractable solid which did not contain acidic compounds. A small quantity of bromotetrafluorobenzoic acid was also isolated from this reaction.

In order to provide sufficient I for immediate Contract requirements impure decafluoro-m-xylene prepared previously (ref. 1) was hydrolysed and the acidic product purified by recrystallisation. The acid obtained by this route, together with that obtained by metalation and carbonation of 1,2,3,5-tetrafluorobenzene, has been sufficient for Monsanto's initial requirements, but a more satisfactory synthesis of I is required and other syntheses are being studied.

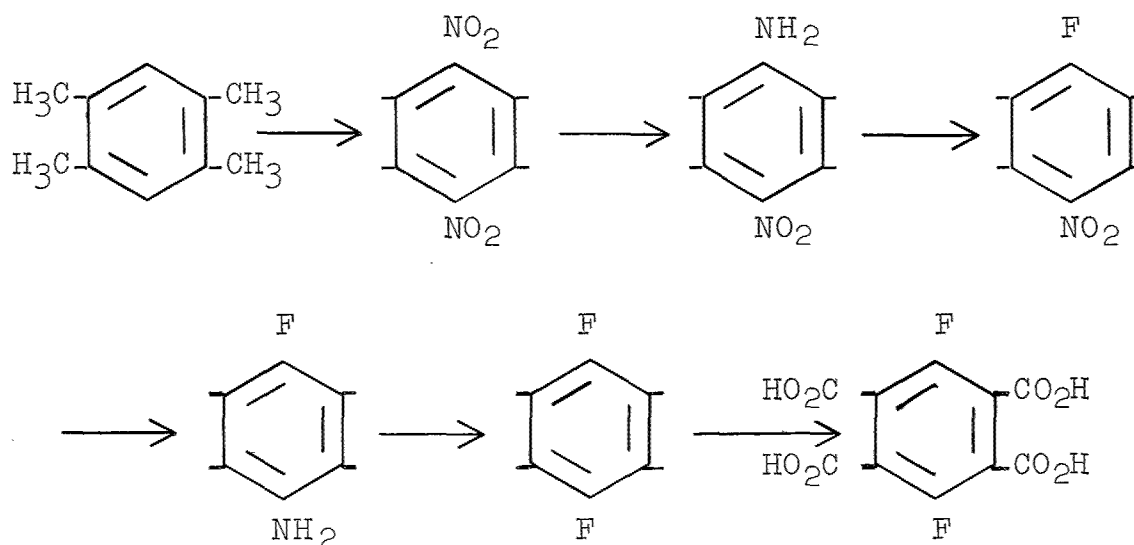
One possibility is fluorination of tetrachloroisophthaloyl chloride with potassium fluoride. Recent Russian work describes the fluorination of tetrachloroterephthaloyl chloride with potassium fluoride or cesium fluoride (ref. 3). In order to try to prepare I similarly, tetrachloro-m-xylene was prepared by nuclear chlorination of m-xylene (ref. 4) and oxidised with dilute nitric acid (ref. 5) to give a 29% yield of tetrachloroisophthalic acid; 51% of the starting material was recovered. Treatment of the acid with phosphorus pentachloride gave tetrachloroisophthaloyl chloride which, when heated with potassium fluoride at 260-270° for 2 hours, gave a water-insoluble product containing 60% of chlorine (tetrafluoroisophthalic acid is soluble in water). Further work is being carried out on this reaction.

Another route under investigation involves the preparation of 3-bromoheptafluorotoluene and its conversion, by cyanation or by means of the Grignard reaction, to 3-trifluoromethyl-2,4,5,6-tetrafluorobenzoic acid, and then by hydrolysis to tetrafluoroisophthalic acid. Bromination of benzotrifluoride gave pentabromobenzotrifluoride in 43% yield. Heating the pentabromide with dry potassium fluoride in tetramethylene sulphone at 230-240° for 8 1/4 hours gave 3-bromoheptafluorotoluene in 11% yield, but it was contaminated with about 23% of an impurity with a similar boiling point, believed to contain hydrogen. Methods of removing this impurity are being studied. The analogous fluorination of pentachlorobenzotrifluoride, studied previously (ref. 6), gave pure 3-chloroheptafluorotoluene, but the chlorine atom was too unreactive for this compound to be of use as an intermediate for I.

## 2. DIFLUOROPYROMELLITIC ACID (II)

Three syntheses of II have been investigated, (a) preparation and oxidation of difluorodurene, (b) fluorination by halogen exchange of derivatives of dichloropyromellitic acid, and (c) cyanation of p-difluorotetrabromobenzene and hydrolysis of the tetracyano-compound.

The first route, outlined schematically below, provides a practicable synthesis of II:-



(The methyl groups have been omitted from the second and subsequent formulae for the sake of clarity).

Nitration of durene, best carried out using fuming nitric acid, gave dinitrodurene in 83% yield. Reduction of dinitro-compound with Raney nickel and hydrazine gave diaminodurene in 87% yield. Attempts to convert the diamine to difluorodurene, either by diazotisation in anhydrous hydrofluoric acid and decomposition of the diazonium fluoride, or by diazotisation in aqueous solution and thence via the diazonium borofluoride, were unsuccessful. In both cases oxidation occurred, resulting in the formation of duroquinone. Sodium polysulphide reduction of dinitrodurene gave 4-amino-1-nitrodurene in 98% yield. This amine was diazotised in anhydrous hydrofluoric acid and the diazonium fluoride decomposed to give 4-fluoro-1-nitrodurene in 75% yield. Reduction of the fluoronitro-compound was best carried out with zinc and hydrochloric acid; an 80-88% yield of 4-amino-1-fluorodurene was obtained. The fluoro-amine was diazotised in anhydrous hydrogen fluoride. Decomposition of the diazonium fluoride gave only a low yield of difluorodurene but a diazonium borofluoride was obtained in the usual way, and was readily decomposed to difluorodurene. Oxidation of difluorodurene with dilute nitric acid (cf ref. 7) yielded difluoropyromellitic acid. Conversion of this acid to the dianhydride is in progress.

The duroquinone obtained as described above was reduced and the resulting durohydroquinone treated with sulphur tetrafluoride in an attempt to form difluorodurene by a shorter route than the one described. However, durohydroquinone did not react with sulphur tetrafluoride in toluene at 100°; at 140-150° extensive decomposition occurred.

Dichlorodurene, formed in 53% yield by nuclear chlorination of durene, was oxidised by dilute nitric acid to dichloropyromellitic acid in 57% yield (ref. 7). Treatment of the acid with diazomethane gave an 89% yield of the tetramethyl ester. No reaction occurred when the ester was heated with anhydrous potassium fluoride at 190° for 10 hours, but extensive decomposition occurred when the reactants were kept at 220° for 5 hours. No product was isolated when the reactants were heated at 180° in tetramethylene sulphone.

Dichloropyromellitic dianhydride, prepared by sublimation of dichloropyromellitic acid, decomposed extensively when heated with potassium fluoride at 250° for 44 hours.

Dichloropyromellitoyl chloride, prepared in 45% yield by treatment of dichloropyromellitic acid with phosphorus pentachloride, melted with decomposition at 265-267°. Consequently the maximum temperature allowable for the reaction of the acid chloride with potassium fluoride was about 250° and the product

from a reaction at this temperature appeared to be dichloro-pyromellitoyl fluoride, no exchange of the nuclear chlorine atoms having occurred.

When 1,2,4,5-tetrabromodifluorobenzene, prepared in 97% yield by bromination of p-difluorobenzene, was heated with cuprous cyanide in refluxing dimethylformamide for 2.5 hours an intractable product was obtained, believed to be the crude tetranitrile. Treatment of this material with concentrated nitric and sulphuric acid and finally with nitrous acid gave crude difluoropyromellitic acid (21% yield from the tetrabromo-compound). The acid could not be purified but was treated with diazomethane in ether to give tetramethyl difluoropyromellitate in low yield, identical with the ester from difluoropyromellitic acid prepared from difluorodurene.

### 3. TETRAFLUORO-m-PHENYLENEDIAMINE (III)

Pentafluoroaniline is deactivated to nucleophilic attack but we have found that when it is treated with ammonium hydroxide solution under forcing conditions (205°/60 hours) a second amino group is introduced. The product was purified by crystallisation and was then believed to be of about 97% purity, on the basis of gas chromatographic and elemental analysis data. However, subsequent examination of a sample by nuclear magnetic resonance and on a Versamid gas chromatography column showed that about 10% of another isomer, probably the para-diamine, was present. Monsanto are attempting to purify the 90% pure meta-diamine we have previously sent to them and we are examining alternative routes to III.

Treatment of decafluorocyclohexene with ammonia and reductive dehydrofluorination of the 1-amino-3-imino-2,4,4,5,5,6,6-heptafluorocyclohexene so formed provides III in low overall yield (ref. 8). We have used this sequence to prepare a pure sample of III for use as a reference compound but the low yield obtained does not encourage us to use this method as a preparative route.

A route to III currently under investigation involves nitration and reduction of 1,2,3,5-tetrafluorobenzene. Nitration of the tetrafluorobenzene with a cold mixture of concentrated sulphuric and nitric acids gave 2,3,4,6-tetrafluoronitrobenzene (ref. 9). It has not proved possible to introduce a second nitro group, either with fuming nitric acid and concentrated sulphuric acid, or by using cupric nitrate in acetic anhydride. Reduction of the nitro-compound with iron filings and ammonium

chloride solution gave 2,3,4,6-tetrafluoroaniline in 85% yield (ref. 9). The amine has been acetylated and attempts are being made to nitrate the resultant 2,3,4,6-tetrafluoroacetanilide.

#### 4. TETRAFLUORO-o-PHENYLENEDIAMINE (IV)

The preparation of this compound was of interest in connection with identifying the impurities formed during the amination of pentafluoroaniline.

Nitration of 1,2,3,4-tetrafluorobenzene at 25-30° gave 2,3,4,5-tetrafluoronitrobenzene in 64% yield. The nitro-group was readily reduced with tin and hydrochloric acid giving 2,3,4,5-tetrafluoroaniline (78% yield). Conversion of the amine to the acetanilide proceeded in 90% yield and nitration of the anilide with a mixture of nitric and sulphuric acids gave 2-nitro-3,4,5,6-tetrafluoroacetanilide (79% yield). Refluxing this compound with 50% sulphuric acid gave a 40% yield of 2-nitro-3,4,5,6-tetrafluoroaniline which was hydrogenated in the presence of Raney nickel to give IV in 74% yield.

#### 5. TETRAFLUORO-p-PHENYLENEDIAMINE (V)

The availability of pentafluorobenzonitrile and the facile para substitution of this compound by nucleophiles prompted its use as the starting point for a synthesis of V. Treatment of the nitrile with concentrated ammonium hydroxide gave 4-amino-2,3,5,6-tetrafluorobenzonitrile (81% yield). Heating the amino-nitrile with 98% sulphuric acid at 80° for 75 minutes yielded p-aminotetrafluorobenzamide in 87% yield. The amide was rearranged to form V in 15% yield by reaction with bromine in sodium hydroxide solution. The efficiency of this last stage was not improved in a larger-scale experiment.

#### 6. TETRA-SUBSTITUTED-HEXAFLUOROBIPHENYLS

Early attempts to prepare 3,4,3',4'-tetraminohexafluorobiphenyl (VI), required for the preparation of a benzimidazole model condensate, were described in a previous Report (ref. 1). A successful synthesis has now been devised starting from readily available 4,4'-diamino-octafluorobiphenyl.

Oxidation of this diamine with trifluoroperacetic acid gave 4,4'-dinitro-octafluorobiphenyl in 60% yield which, either by treatment with gaseous ammonia, or by the action of concentrated ammonium hydroxide in dioxan solution, gave 3,3'-diamino-4,4'-dinitrohexafluorobiphenyl. Reduction of the diaminodinitro-hexafluorobiphenyl with hydrogen in the presence of Raney nickel at atmospheric pressure gave VI in 39% yield. The disposition of the four amino groups was confirmed by N.M.R. spectroscopy. The formation of a bis-quinoxalyl derivative by treatment of the tetramine with benzil provided further evidence in support of the presence of two pairs of amino groups on adjacent carbon atoms.

3,3'-Dihydroxy-4,4'-diaminohexafluorobiphenyl (VII), required for the preparation of an oxazole model, was obtained in 63% yield by reduction of 3,3'-dihydroxy-4,4'-dinitrohexafluorobiphenyl with hydrogen in the presence of Raney nickel catalyst. The 3,3'-dihydroxy-4,4'-dinitrohexafluorobiphenyl was prepared by treating 4,4'-dinitrooctafluorobiphenyl with either sodium hydroxide in aqueous dioxan or with potassium hydroxide in t-butanol. The latter is the preferred reagent giving the dihydroxy-compound in 61% yield. The two hydroxyl groups are likely to be in the 3,3'-positions (cf. the formation of 3,3'-diamino-4,4'-dinitrohexafluorobiphenyl from 4,4'-dinitrooctafluorobiphenyl) but this configuration has yet to be confirmed.

The reaction of 4,4'-dinitrooctafluorobiphenyl with sodium hydrogen sulphide is being tried as a route to 3,3'-dimercapto-4,4'-dinitrooctafluorobiphenyl (VIII), required for reduction to the dimercaptodiamino-compound, which will be used for the preparation of a thiazole model. A preliminary reaction of 4,4'-dinitrooctafluorobiphenyl with an ethanolic solution of sodium hydrogen sulphide gave a product, believed to be impure VIII. Further work on this reaction is in progress.

## 7. FLUOROAROMATIC SECONDARY AMINES

Highly fluorinated aromatic secondary amines are required for the preparation of amide models which do not contain any hydrogen on the nitrogen atoms. The presence of such hydrogen is thought to be responsible for the  $T_D$  of fluorinated amide models of the type  $C_6F_4(CONHC_6F_5)_2$  being below that of the hydrogenic analogue (ref. 1). It was agreed with Monsanto that the synthesis of decafluorodiphenylamine (IX) and 1,4-bis(pentafluoro-anilino)tetrafluorobenzene (X) should be attempted.

The reaction of hexafluorobenzene with sodamide in liquid ammonia, which gave a low yield of IX has been described by Brooke et al. (ref. 10). Recently, Burdon et al. (ref. 11) obtained IX in 15% yield by treating hexafluorobenzene with the sodio-derivative of pentafluoroaniline in liquid ammonia. We now find that hexafluorobenzene in boiling dioxan reacts with the sodio-derivative of pentafluoroaniline forming decafluorodiphenylamine in 40% yield.

Attempts to prepare X by treating decafluorodiphenylamine with the sodio-derivative of pentafluoroaniline gave only a trace of a compound believed to be X on the basis of infra-red evidence and elemental analysis, despite the use of forcing conditions (6 hours at 170° in an autoclave). When even more vigorous conditions (220° for 4 1/2 hours) were employed little improvement in yield was effected.

#### 8. TETRAFLUORORESORCINOL (XI)

Initial attempts to prepare XI were directed towards the substitution of iodine atoms in iodopolyfluorobenzenes with groups which could be hydrolysed to hydroxyl. In trial experiments, iodopentafluorobenzene was reacted with fluoro-, and with chloro-sulphonic acid in unsuccessful attempts to make fluoro- and chloro-sulphates. Also unsuccessful were attempts to make pentafluorophenyl toluene-p-sulphonate by reaction of iodopentafluorobenzene with silver toluene-p-sulphonate in dimethylformamide or acetonitrile solution.

Substitution of bromine atoms in bromofluorobenzenes with hydroxyl groups by treatment with an aqueous suspension of potassium fluoride and cuprous oxide at about 200° under autogenous pressure was tried. Vorozhtsov et al. (ref. 12) used this method for preparing mono-, di-, and tri-fluorophenols from the corresponding bromofluorobenzene. In our experiments yields of from 2-16% of pentafluorophenol were obtained from bromopentafluorobenzene under various conditions, but 1,3-dibromotetrafluorobenzene gave only intractable polymeric material.

Introduction of a second hydroxyl group into pentafluorophenol was studied next. A reaction of potassium hydroxide with pentafluorophenol in t-butanol was tried on the grounds that t-butanol is a good solvent for potassium pentafluorophenate. Further, since the hydroxyl ion is not appreciably solvated in this solvent, it should behave as a strong nucleophile. However no reaction occurred when pentafluorophenol was heated with potassium hydroxide in refluxing t-butanol for 33 hours.



While this work was in progress Wall (ref. 13) reported that he had obtained XI by heating hexafluorobenzene with an aqueous solution of potassium hydroxide under autogenous pressure at 150°. We repeated Wall's experiment and obtained a small yield of material believed to be tetrafluororesorcinol. However, when pentafluorophenol was heated under similar conditions (150°/5 hours) with three equivalents of potassium hydroxide, tetrafluororesorcinol was formed in 47% yield (53% conversion). The meta orientation of the hydroxyl groups was confirmed by N.M.R. spectroscopy and by the preparation of a bis(toluene-p-sulphonate) having a different melting point to those of the bis(toluene-p-sulphonates) prepared from tetrafluorohydroquinone and tetrafluorocatechol (ref. 14).

## 9. PERFLUOROAROMATIC THIOETHERS

Robson et al. (ref. 15) attempted to prepare bis(pentafluorophenyl)sulphide by treating hexafluorobenzene in pyridine with potassium pentafluorothiophenate, but isolated only polymeric material considered to be a perfluoropoly(phenylene sulphide). Recent work by Imperial Smelting has shown that perfluoroaromatic thioethers are readily prepared by the method described by Adams et al. (refs. 16, 17) for the preparation of the hydrogenic analogues. Thus, cuprous pentafluorothiophenate, prepared from cuprous oxide and pentafluorothiophenol in ethanol, reacts with 1,4-dibromotetrafluorobenzene, 1,3-dibromotetrafluorobenzene and 4,4'-dibromooctafluorobiphenyl in dimethylformamide to form 1,4-bis(pentafluorophenylthio)tetrafluorobenzene (XII), 1,3-bis(pentafluorophenylthio)tetrafluorobenzene (XIII), and 4,4'-bis(pentafluorophenylthio)octafluorobiphenyl (XIV), respectively. Experimental details for the preparation of these compounds are given in this Report but their characterisation by desulphurisation and other reactions is not given here as it will be published elsewhere. Samples of XII, XIII and XIV, purified by recrystallisation to constant melting point, were used by Monsanto for  $T_D$  determination.

## 10. PERFLUOROAROMATIC DITHIOLS

Attempts to prepare tetrafluorobenzenedithiol by treating hexafluorobenzene with sodium hydrosulphide gave only polymeric material (ref. 15). We are attempting to prepare tetrafluorobenzene-1,4-dithiol by demethylation of 1,4-bis(methylthio)tetrafluorobenzene (XV). Preparation of XV has been accomplished in two ways: (1) by reaction of cuprous thiomethylate with

1,4-dibromotetrafluorobenzene which gave the product in 76% crude yield but in only 20% yield after purification, (2) by reaction of sodium thiomethylate with hexafluorobenzene. This latter procedure was more convenient and gave pure XV in 51% yield. So far attempts to demethylate XV have been unsuccessful. For example, after treatment with hydrogen bromide in refluxing acetic acid for 10 hours the starting material was recovered. Treatment of XV with 20% oleum, a method previously used for demethylating fluoroaromatic ethers (ref. 15), did not bring about reaction. Treatment of XV with 65% oleum yielded only a polymeric alkali-insoluble material, while the action of 43% oleum, and stabilised sulphur trioxide respectively, gave only small amounts of viscous oils of complex composition. When XV was treated with sodium in liquid ammonia either starting material was recovered, when a deficiency of sodium was used, or ammination occurred concurrently with demethylation yielding complex products.

#### 11. OCTAFLUORONAPHTHALENE (XVI)

This compound was prepared to fulfil a requirement by U.S.A.F. The method used was devised earlier by Imperial Smelting (ref. 18).

## D. EXPERIMENTAL

### 1. TETRAFLUOROISOPHTHALIC ACID

#### a. Large-Scale Preparation from 1,2,3,5-Tetrafluorobenzene by Metalation and Carbonation

(1) Butyl Lithium n-Butyl chloride (370g., 4.0 mole) was dissolved in hexane (400 ml.) and 5 ml. added to lithium sand (72g.) in hexane at 15°. After a few minutes the temperature rose to 30° and the remainder of the butyl chloride/hexane mixture was run in dropwise over 3 hours maintaining a gentle reflux. The mixture was refluxed for 10 hours, allowed to cool and filtered under nitrogen through a glass wool plug. The filtrate was decanted from a heavier residue and an aliquot analysed. The yield of n-butyl lithium was 141g., 55%.

(2) Metalation and Carbonation of 1,2,3,5-Tetrafluorobenzene Tetrahydrofuran (2000 ml.) was added to n-butyl lithium (141g., 2.2 mole) in hexane (1 liter) at -60°. 1,2,3,5-Tetrafluorobenzene (165g., 1.1 moles) was added over 100 minutes at -55° to -60° and the mixture stirred for 1 hour at that temperature. A slurry of solid carbon dioxide (300g.) in tetrahydrofuran (100 ml.) was added rapidly with stirring and the mixture was allowed to warm to room temperature. Concentrated hydrochloric acid (400 ml.) and water (600 ml.) were added and the mixture steam distilled to remove tetrahydrofuran and hexane. The solution remaining contained a brown intractable gum which was discarded. Exhaustive ether extraction of the aqueous solution and evaporation of the ether gave a residue which was extracted with benzene. On concentrating the benzene extract crude tetrafluoroisophthalic acid (21.0g.), m.p. 195°-210°, crystallised. Recrystallisation twice from nitrobenzene gave 14.3g., m.p. 216-220°, with a correct infra-red spectrum.

The benzene solution remaining after crystallisation of the tetrafluoroisophthalic was evaporated to dryness yielding 2,3,4,6-tetrafluorobenzoic acid (7.9g., 3.7%). Recrystallisation from water gave 3.0g., m.p. 100.5°-102°.

Anal. Calc'd. for  $C_7H_2F_4O_2$ : C, 43.3; H, 1.0; F, 39.2%

Found: C, 43.4; H, 0.9; F, 38.1

b. Attempted Conversion of 1,3-Dibromotetrafluorobenzene to Tetrafluoroisophthalic Acid via a Dilithio-derivative

A solution of butyl lithium was prepared from lithium sand (8g., 1.13g. atom) and butyl bromide (69g., 0.50 mole) in ether (250 ml.) and filtered under nitrogen to remove the excess of lithium. The filtrate (190 ml.) was found to contain 0.47 mole of butyl lithium by titration of an aliquot against 0.1 N hydrochloric acid.

The butyl lithium solution was stirred and maintained at  $-60^{\circ}$  while tetrahydrofuran (500 ml.) and then 1,3-dibromotetrafluorobenzene (70g., 0.23 mole) were added. The mixture was kept at  $-60^{\circ}$  for 30 mins., then carbon dioxide was bubbled through for 1.5 hours at  $-60^{\circ}$  and for a further time while the mixture warmed to room temperature. Water (400 ml.) and 11N hydrochloric acid (200 ml.) were added. The mixture was steam distilled. A brown resinous solid (40g.) remained. No acidic material was extracted by treating it with sodium hydroxide solution. The solid could not be sublimed or otherwise purified. Exhaustive ether extraction of the aqueous liquors remaining after steam distillation gave a pale brown solid (5g.), m.p.  $88-92^{\circ}$ . Recrystallisation from  $80-100^{\circ}$  petrol ether raised the melting point to  $95-96^{\circ}$ . This solid is bromotetrafluorobenzoic acid.

Anal. Cald'd. for  $C_7HBrF_4O_2$ : C, 30.8; H, 0.4%

Found: C, 30.7; H, 0.4

c. From Tetrachloroisophthalic Acid

(1) Tetrachloro-m-xylene A preliminary experiment showed that only partial chlorination occurred when m-xylene (200g.) in carbon tetrachloride was chlorinated at reflux for 24 hours. A longer chlorination period was therefore used.

m-Xylene (226g., 2.13 mole), dissolved in carbon tetrachloride (1 liter) containing ferric chloride (5g.) and iron filings (5g.), was chlorinated at reflux temperature for 48 hours. After 32 hours solid material separated. The final mixture was filtered hot. The residue of crude tetrachloroxylene (197g.) was washed with carbon tetrachloride. On cooling, the filtrate deposited crystals of tetrachloroxylene and concentration gave a further crop. The yield was 353.6g., 68%. Recrystallisation from benzene gave 323g., m.p.  $227-229^{\circ}$ . A small sample was sublimed for analysis.

Anal. Calc'd. for  $C_8H_6Cl_4$ : C, 39.4; H, 2.5%

Found: C, 39.6; H, 2.7

(2) Tetrachloroisophthalic Acid      Tetrachloro-m-xylene  
(97.6g., 0.4 mole), nitric acid (150 ml., s.g. 1.42) and water (450 ml.) were heated in a stainless steel autoclave at 180°-200° with agitation for 4 hours. The cold autoclave was vented to remove nitrogen oxides, the contents diluted with water, the solid product collected, washed with water and dried. The product (96.3g.), m.p. 185-260°, was fractionally crystallised from aqueous ethanol to give crude tetrachloro-m-xylene (49.5g.), m.p. 200-210°, and tetrachloroisophthalic acid (35.7g., 29%), m.p. 285-290°. Recrystallisation of the crude acid from water raised the melting point to 299-303°.

Anal. Calc'd. for  $C_8H_2Cl_4O_4$ : C, 31.6; H, 0.75; Cl, 46.7%

Found: C, 31.6; H, 0.8; Cl, 46.8

(3) Tetrachloroisophthaloyl Chloride      Tetrachloro-isophthalic acid (10g.) and phosphorus pentachloride (17g.) were heated on a steam bath until reaction had ceased. The homogeneous mixture was kept at 80°/15 mm. to remove volatile products. The residue was tetrachloroisophthaloyl chloride.

(4) Attempted Preparation of Tetrafluoroisophthaloyl Fluoride      Tetrachloroisophthaloyl chloride was heated for 2 hours at 260-270° with dry potassium fluoride (25g.) in a 50 ml. autoclave. The product was exhaustively extracted with ether. Evaporation of the extract gave water-insoluble material (6.1g.) (tetrafluoroisophthalic acid is soluble in water) which was sublimed and recrystallised from aqueous ethanol giving a white solid, m.p. 96-97.5°.

#### d. Hydrolysis of Impure Decafluoro-meta-xylene

The decafluoro-m-xylene used for this experiment was prepared by defluorination of perfluoro(1,3-dimethylcyclohexane) as described earlier (ref. 1). It contained about 76% of the meta-isomer and about 7% of another isomer, probably the para-isomer.

Impure decafluoro-m-xylene (50g.) and 40 ml. of 20% oleum were shaken in a 100 ml. glass ampoule at 150° for 12 hours. The product was poured on to ice. Exhaustive ether extraction of the resulting solution gave a solid which, after being dried at 80° for 2 hours, weighed 37.3g., m.p. 210-215°. It was combined with a similar product (39.0g.) from another experiment in which 62g. of xylene were hydrolysed. Recrystallisation of

64.3g. of the product from 300 ml. of a 1:1 mixture of ether and 40-60° petrol ether gave 27.2g. of tetrafluoroisophthalic acid, m.p. 215-216.5°.

Anal. Calc'd. for  $C_8H_2F_4O_2$ : C, 40.3; H, 0.8; F, 31.9%

Found: C, 40.2; H, 1.0; F, 31.4

The infra-red spectrum (No. 2815) of this product was very similar to that of a spectrum of an authentic sample prepared by hydrolysis of decafluoro-m-xylene, supplied by Birmingham University.

Concentration of the mother liquors afforded two further crops of crystals, 9.1g., m.p. 213.5-214.5 and 6.7g., m.p. 210-212°. Taking the mother liquor to dryness left 20.6g., m.p. approx. 180-205°.

e. Preparation via 3-Bromoheptafluorotoluene

(1) Pentabromobenzotrifluoride To benzotrifluoride (48.7g., 0.33 mole) and bromine (357g., 4.5 mole) was added 65% oleum over 70 minutes, the temperature being kept at 15-20°. The dark brown solid product was washed with sodium metabisulphite solution then with water and the tan material (80g.) recrystallised from ethanol yielding pentabromobenzotrifluoride (63g., 35%), m.p. 170-173°. A further recrystallisation of a sample raised the melting point to 173-176°.

Anal. Calc'd. for  $C_7Br_5F_3$ : C, 15.6; Br, 73.9; F, 10.5%

Found: C, 15.7; Br, 73.6; F, 10.4

The infra-red spectrum (No. 3353) did not contain bands assigned to aromatic C-H absorptions.

A large-scale preparation using 438g. (3.0 mole) of benzotrifluoride gave pentabromobenzotrifluoride 690g. (43%), m.p. 167.5-170°, 97% pure by gas chromatography.

(2) Fluorination of Pentabromobenzotrifluoride with Potassium Fluoride in Tetramethylene Sulphone Pentabromobenzotrifluoride (747g., 1.38 mole) was added to dry potassium fluoride (806g., 13.9 mole) in tetramethylene sulphone (2.5 kg.) and the mixture stirred and heated at 230-240° for 8 1/4 hr. The mixture progressively darkened to a black colour and volatile material (203g.) was distilled out (b.r. 140-180°). Further distillation under reduced pressure yielded only tetramethylene sulphone.

Fractionation of the crude product through an 18 x 1.5 cm. helices-packed column gave a fraction (60.3g.), b.p. 152-154°/-771.3 mm., which, by gas chromatography, contained 3-bromoheptafluorotoluene (77%) and an unknown material (23%). The infrared (No. 3389) of this compound contained bands assigned to C-H stretching vibrations.

## 2. DIFLUOROPYROMELLITIC ACID

### a. Preparation via Difluorodurene

(1) Dinitrodurene Powdered durene (500g.) was added portionwise over a period of 1 hour to fuming nitric acid (2.5l., s.g. 1.51). The first 350g. was added at 13-16° and the remaining 150g. at 16-18°. The mixture was maintained at about 18° for a further 30 minutes and then poured into iced water (8l.). The precipitate was collected, washed and dried. There was obtained 820g. of impure dinitrodurene, m.p. 202-210°. Recrystallisation from acetone gave 694g. (83% yield), m.p. 213-215°, and a further crop (60g.), m.p. 200-206°.

(2) Diaminodurene (typical experiment) To a refluxing mixture of dinitrodurene (270g., 1.21 mole), ethanol (2.5l.) and Raney nickel (30g.) was added hydrazine hydrate (360 ml.) during 1.75 hours. The mixture was refluxed for 0.5 hours longer, filtered hot and the filtrate concentrated. The crystals which formed were recrystallised from ethanol giving diaminodurene (173g., 87% yield), m.p. 153.5-154.5°, Smith and Dobrovolsky cited m.p. 149° (ref. 19).

### (3) Attempted Conversion of Diaminodurene to Difluorodurene

(a) By Diazotisation in Anhydrous Hydrofluoric Acid (AHF) Diaminodurene (16.4g., 0.10 mole) and AHF (50 ml.) were stirred in a polythene vessel at -5° and crushed sodium nitrite (13.8g., 0.20 mole) was added in small portions. The mixture was warmed to 70° and kept at 70° for 0.5 hours, then cooled, poured on to ice and neutralised (NaOH). A solid formed and was filtered off. The organic material was leached from sodium fluoride by hot ethanol. The ethanol was diluted with an equal volume of water, the solution depositing crystals on cooling. Sublimation of the crystals gave yellow needles (5.9g.) of duroquinone, m.p. 112-113.5°. A potassium fusion confirmed that the product did not contain nitrogen or fluorine.

In a similar experiment using the same quantities, but in which the diamine was added to AHF and sodium nitrite at  $-10^{\circ}$ , duroquinone (11g.) was obtained.

(b) Via the Diazonium Fluoroborate To a stirred mixture of diaminodurene (16.4g., 0.10 mole), 11N hydrochloric acid (60 ml.) and water (60 ml.) cooled to  $-5$  to  $0^{\circ}$  was added dropwise a solution of sodium nitrite (13.8g., 0.20 mole) in water (30 ml.). Then a solution of sodium fluoroborate (30g., 0.27 mole) in water (100 ml.) was added dropwise and the mixture stirred at  $0^{\circ}$  for 0.5 hours. The solid which formed was collected and extracted with ethanol giving duroquinone, m.p.  $110-112^{\circ}$ .

In a similar experiment, but adding the diamine to a solution of nitrous acid, duroquinone was again produced.

(4) Durohydroquinone Sulphur dioxide was passed into a refluxing solution of duroquinone (27g., 0.16 mole) in ethanol (175 ml.) and water (27 ml.) for 4 hours. The precipitate was filtered off and dried. It weighed 16.2g., 62% yield, m.p.  $235-238^{\circ}$ . Addition of water to the filtrate gave a further 4.0g., m.p.  $233-235^{\circ}$ , Smith and Dobrovolny cited m.p.  $226^{\circ}$  (ref. 19).

(5) Reaction of Durohydroquinone with Sulphur Tetrafluoride

(a) At  $100^{\circ}$  and  $190^{\circ}$  in Absence of Solvent Durohydroquinone (16.6g., 0.1 mole) and sulphur tetrafluoride (25g., 0.23 mole) were heated in an autoclave for 10 hours at  $100^{\circ}$ . The vented gases were passed through sodium hydroxide solution and the residue was washed with an aqueous solution of sodium hydroxide and filtered. Ether extraction of the solid gave only duroquinone.

Heating the same quantities at  $190^{\circ}$  for a short period, and then at  $140^{\circ}$  for 16 hours gave only carbonised product (22g.) from which no organic material was isolatable.

(b) In Toluene Durohydroquinone (11g., 0.066 mole) in toluene (25 ml.) and sulphur tetrafluoride (25g., 0.23 mole) were heated at  $150^{\circ}$  for 10 hours in an autoclave. Extensive carbonisation occurred and no product was isolated.

(6) 4-Amino-1-nitrodurene A solution of sodium polysulphide was prepared from hydrated sodium sulphide (2450g.), sublimed sulphur (315g.) and water (31.).

Half of the solution was added over 15-20 minutes to a solution of dinitrodurene (352g.) in refluxing ethanol (41.).



The mixture was refluxed for a further 15 minutes and was then concentrated until 3.5l. of distillate had collected. Water (500 ml.) was added and the solution was allowed to cool and crystallise. Filtration gave nearly pure aminonitrodurene, m.p. 163-165°.

The remaining sodium polysulphide was used to reduce a second portion of dinitrodurene (352g.). The yield of aminonitrodurene from both experiments was 566g. (93%).

(7) 4-Fluoro-1-nitrodurene Aminonitrodurene (290g.) was added to anhydrous hydrogen fluoride at  $0 \pm 5^\circ$ . The resulting solution was diazotised at  $0 \pm 5^\circ$  by the addition of sodium nitrite (106g.) in small portions over 1 hour. The mixture was stirred at  $0^\circ$  for 1 hour and allowed to warm to room temperature overnight. The excess of hydrogen fluoride was removed at room temperature in a stream of dry air. Water (500 ml.) was added to the residue, the solid product was filtered off, washed with water and recrystallised from methylated spirits (800 ml.) yielding 231g. (77%) of 98% 4-fluoro-1-nitrodurene.

Another preparation using 276g. of aminonitrodurene gave 212g. (75%) of 99% 4-fluoro-1-nitrodurene.

(8) 1-Amino-4-fluorodurene Hydrochloric acid (60 ml., s.g. 1.19) was added portionwise over 10 minutes to a stirred mixture of granulated tin (20g.) and fluoronitrodurene (10g.) in boiling glacial acetic acid (60 ml.). The mixture was refluxed for 30 minutes and then cooled. A solution of sodium hydroxide (65g.) in 65 ml. of water was added and the aminofluorodurene (5.7g.) isolated by steam distillation. Extraction of the aqueous phase with ether gave a further portion (1.4g.). Total yield: 7.1g., (83%).

The reaction was repeated twice using:-

(a) fluoronitrodurene (220g.), tin (440g.), hydrochloric acid (1320 ml.), acetic acid (1320 ml.). Yield: 150g., (80.5%).

(b) fluoronitrodurene (215g.), tin (430g.), hydrochloric acid (1290 ml.), acetic acid (1290 ml.). Yield: 160g., (88%).

(9) Diazotisation of Aminofluorodurene in Anhydrous Hydrogen Fluoride Aminofluorodurene (90g.) was dissolved in anhydrous hydrogen fluoride (750 ml.) at  $0 \pm 5^\circ$ . The solution was diazotised at  $0^\circ$  by the addition of solid sodium nitrite (38g.) over 1 hour, then heated slowly to  $60^\circ$  to remove hydrogen

fluoride. Water (500 ml.) was added and the solid (48g.) filtered off. It was shown by gas chromatography to contain difluorodurene (17%), duroquinone (70%) and aminofluorodurene (13%).

The product was dissolved in ether and the duroquinone removed by extraction with a solution of sodium dithionite in sodium hydroxide. The aminofluorodurene was removed by extraction with 1N hydrochloric acid. The ether was taken off and the residue distilled to give crude difluorodurene. Recrystallisation from methylated spirits yielded 0.1g., m.p. 50-52°.

Anal. Calc'd. for  $C_{10}H_{12}F_2$ : C, 70.5; H, 7.1; F, 21.3%

Found: C, 69.7; H, 7.0; F, 19.9

(10) 4-Fluorodurenediazonium Borofluoride Aminofluorodurene (8.35g.) was dissolved in hot dilute sulphuric acid (8 ml. conc. acid, 30 ml. water). The solution was cooled rapidly to 0° and maintained at  $0 \pm 5^\circ$  whilst a solution of sodium nitrite (3.45g.) in water (10 ml.) was added dropwise. The mixture was stirred at 0° for 30 minutes, then a solution of sodium fluoroborate (8g. in 15 ml. water) was added and the mixture stirred at 0° for a further 30 minutes. The diazonium borofluoride was collected and washed with cold 10% sodium fluoroborate solution. Yield: 8.3g. (62%), m.p. 92° (decomp.).

Anal. Calc'd. for  $C_{10}H_{12}BF_5N_2$ :  $BF_3$ , 25.6%

Found:  $BF_3$ , 25.1

A second diazotisation gave the borofluoride 12.0g. (91%).

Diazotisation using hydrochloric acid (14.5 ml.) instead of sulphuric acid, and with addition of sodium fluoroborate before diazotisation gave a lower yield, 4.5g. (34%).

(11) Pyrolysis of 4-Fluorodurenediazonium Borofluoride 4-Fluorodurenediazonium borofluoride (5g.) was mixed with an equal volume of silica sand and gently heated until gas evolution stopped. From the residue difluorodurene (2.8g., 87%), m.p. 59-61°, 99% purity by gas chromatography, was isolated by sublimation. (I.R. Spectrum No. 3284).

Difluorodurene (Larger-scale preparation) Aminofluorodurene (285g.) was divided into three portions and each portion diazotised in sulphuric acid (46 ml. in 285 ml. water) with sodium nitrite solution (39g. in 115 ml. water). The diazonium borofluoride was precipitated with sodium borofluoride (91g. in 170 ml. water) as described above.

The fluorodurenediazonium borofluoride was decomposed in 40g. portions by heating gently with silica sand (80g.), followed by sublimation as described above. The sublimate of difluorodurene were combined and recrystallised from methylated spirits to give 146g., 49%, m.p. 59-61°.

(12) Difluoropyromellitic Acid and Anhydride Difluorodurene (10g., 0.06 mole) and 25% nitric acid (240 ml.) were heated in a stainless steel autoclave to 180° during 2 hours and maintained at 180° for a further 3 hours. The mixture was continuously extracted with ether. Evaporation of the extract gave difluoropyromellitic acid (3g., 17.6%), which, after recrystallisation from water, gave the pure acid (1.0g.), m.p. 270° (decomp.).

Anal. Calc'd. for  $C_{10}H_4F_2O_8$ : C, 41.4; H, 1.4; F, 13.1%; equiv. 72.5

Found: C, 41.2; H, 1.4; F, 13.1; equiv. 72.4

Oxidation of difluorodurene (144g.) in batches of 25g. with 25% nitric acid and treatment of the reaction product as described above yielded pure difluoropyromellitic acid (35g.) (I.R. No. 3351).

Treatment of a solution of difluoropyromellitic acid (2.0g.) in ethanol (10 ml.) at room temperature with a solution of diazomethane (1.44g.) in ether (130 ml.) followed by stirring for 30 minutes and evaporation of the solvents yielded white crystals of tetramethyl difluoropyromellitate (1.3g., 55%), m.p. 120-121°, identical with the compound prepared via cyanation of 1,4-difluorotetrabromobenzene.

Anal. Calc'd. for  $C_{14}H_{12}F_2O_8$ : C, 48.5; H, 3.5; F, 11.0%

Found: C, 48.6; H, 3.6; F, 10.2

(I.R. No. 3376, 3376A)

Difluoropyromellitic acid (35g.) and acetic anhydride (200g.) were refluxed for 3 hours. The acetic acid formed (21 ml., 91% theory) was removed by fractional distillation and the remaining acetic anhydride was distilled under vacuum. The residue was recrystallised from acetic anhydride to give 15g. of product, believed to be the dianhydride. Purification of this product is being carried out.

b. Preparation via Halogen Exchange on Derivatives of Dichloropyromellitic Acid

(1) Dichlorodurene Dry chlorine was passed for 1 3/4 hours into a well stirred solution of durene (103g., 0.77 mole) and iodine (13g.) in 40-60° petrol ether maintained at 20°. The solution remained clear but on raising the temperature to 25° a rapid deposition of white crystals occurred. Chlorine was passed for a further 1/2 hour, the solution filtered and the product washed with 40-60° petrol ether and dried in vacuo over phosphoric oxide giving dichlorodurene (82g., 53%), m.p. 185°-187.5°. (Lit. value m.p. 191°, ref. 7). A sample recrystallised from ethanol had m.p. 192-193.5° and was 97.2% pure by gas chromatography.

(2) Dichloropyromellitic Acid Crude dichlorodurene (25g., 0.12 mole), m.p. 185°-187.5°, and 500 ml. 25% HNO<sub>3</sub> (d, 1.147) in a 900 ml. capacity stainless steel autoclave were heated to 180° in 2 hours and shaken at that temperature for a further 3 hours. After cooling, the nitrogen oxides were vented and the contents, a slurry of pearly plates in a green solution, filtered. The crystals were washed with ice-water giving crude product (34g.). Recrystallisation from boiling water (150 ml.) gave white crystals of dichloropyromellitic acid (22.0g., 57%), m.p. > 300°.

(3) Tetramethyl Dichloropyromellitate To a solution of dichloropyromellitic acid (9.60g., 0.03 mole) in dry ether (250 ml.) at 0° was added dropwise during 15 minutes a cold ethereal diazomethane solution (approx. 5.5g. in 200 ml. ether), with frequent shaking of the mixture. Vigorous gas evolution occurred (with deposition of a white solid) and a yellow colour persisted after all diazomethane had been added. Solvent removal yielded a buff residue (10.02g., 89% crude yield) and recrystallisation from acetone (250 ml.) gave white crystals of the tetramethyl ester (6.5g.), m.p. 177-178.5° (lit. value 175°. Ref. 7).

Anal. Calc'd. for C<sub>14</sub>H<sub>12</sub>Cl<sub>2</sub>O<sub>8</sub>: C, 44.3; H, 3.2; Cl, 18.7%

Found: C, 43.9; H, 3.2; Cl, 18.5

(Infra-red No. 3137)

(4) Attempted Halogen Exchange Reactions on the Ester

(a) At 220° The tetramethyl ester (1.0g., 0.003 mole) and anhydrous potassium fluoride (0.64g., 0.01 mole) were heated under nitrogen in a 60 ml. capacity stainless steel autoclave for 5 hours at 220°. When cool the autoclave was vented,

CO and CO<sub>2</sub> being detected in the exit gases, and the contents, a pasty brown mass (1.51g.), acetone extracted for 4 hours in a Soxhlet extractor. The inorganic residue (0.55g.) was dissolved in water to give a chloride ion-free solution. The acetone extract was evaporated to small volume in vacuo and deposited crystals (0.21g.), m.p. 165-175, which contained chlorine but not fluorine. Recrystallisation gave the unchanged tetramethyl ester, m.p. 177-178°, undepressed in admixture with the starting material, and having an identical infra-red spectrum. Evaporation of the residual acetone solution after filtration of the deposited crystals yielded a viscous residue (0.41g.), containing chlorine but not fluorine, which was probably impure ester.

(b) At 190° The tetramethyl ester (3.0g., 0.009 mole) and anhydrous potassium fluoride (2.2g., 0.03 mole) were heated for 10 hours at 190° in the manner described in (a) above. The vented exit gases contained a little CO<sub>2</sub> and no CO. Continuous ether extraction of the crude product (4.94g.) for 19 hours and evaporation of the extract gave tan crystals (2.88g.), m.p. 166°-172°, containing chlorine but no fluorine. Recrystallisation gave the unchanged ester (2.5g.), m.p. 178-179.5°, undepressed in admixture with authentic material. The inorganic residue from the extractor (2.0g.) gave a weak positive chloride ion test in aqueous solution.

(c) In Tetramethylene Sulphone at 150° and 210° The tetramethyl ester (2.7g., 0.009 mole) and anhydrous KF (1.7g., 0.028 mole) were stirred and heated in tetramethylene sulphone (50 ml.) under anhydrous conditions. After 4 hours at 150° very little darkening had occurred and the temperature was raised to 210° over 15 minutes when rapid darkening occurred accompanied by evolution of gases. The temperature was lowered to 180° and held there a further 6 hours. The cooled black reaction mixture was poured onto ice (100g.), diluted to 250 ml. and filtered to remove the dark brown precipitate. Acetone extraction of the precipitate in a Soxhlet extractor and evaporation of the extract in vacuo yielded a dark brown residue (0.9g.) which could not be recrystallised and did not contain fluorine.

(5) Dichloropyromellitic Dianhydride Dichloropyromellitic acid (1g., 0.003 mole) was sublimed four times at 0.1 mm. and 240-250° giving pale yellow crystals (0.58g.), m.p. > 300° (lit. value 265-70°). (Ref. 7).

Anal. Calc'd. for C<sub>10</sub>Cl<sub>2</sub>O<sub>6</sub>: C, 41.84; Cl, 24.73%

Found: C, 38.5; Cl, 23.5

In a larger-scale preparation the acid (10g., 0.03 mole) was sublimed twice at 240°/0.1 mm. yielding the dianhydride (6.8g., 78% yield).

(6) Attempted Fluorination of Dichloropyromellitic Dianhydride Dichloropyromellitic dianhydride (6.8g., 0.024 mole) and anhydrous potassium fluoride (5.5g., 0.096 mole) were thoroughly mixed and further dried on a vacuum hotplate at 150° and 0.1 mm. for 7 hours. The mixture was rapidly charged into a 60 ml. capacity stainless steel autoclave and heated under nitrogen for 44 hours at 250°. When cool it was noted that a four-fold pressure increase had occurred. The vented gases contained much carbon monoxide and carbon dioxide, and the product was very dark. Sublimation of the crude product at 220° and 0.1 mm. gave yellow crystals (0.51g.), m.p. 300°, containing chlorine but not fluorine and having a very similar infra-red to that of the starting material. Continuous acetone extraction of the remaining carbonaceous material (12g.) for 6 hours gave on solvent removal, viscous material (0.5g.) containing chlorine but not fluorine.

(7) Dichloropyromellitoyl Chloride Dichloropyromellitic acid (9.6g., 0.03 mole) and phosphorus pentachloride (25.0g., 0.12 mole) were kept at 160-170° until hydrogen chloride evolution had ceased (26 hours). Phosphorus oxychloride (15.6g., 0.10 mole) was distilled off and the residue (8.86g.) was continuously ether extracted for 30 hours. Non-extracted material (5.28g., 45% yield), m.p. 258-275°, remained and was shown by an infra-red spectrum to have carbonyl absorptions attributable to the acid chloride group. Some dichloropyromellitic acid was also present. The extracted material was largely unreacted dichloropyromellitic acid. Recrystallisation of a sample of the crude acid chloride from nitrobenzene gave pale yellow crystals of dichloropyromellitoyl chloride, m.p. 265-267° (decomp.).

Anal. Calc'd. for  $C_{10}Cl_6O_4$ : C, 30.3; Cl, 53.6%

Found: C, 30.4; Cl, 52.4

Treatment of a small sample (ca. 0.25g.) of the crude acid chloride with methanol (1 ml.) and pyridine (0.5 ml.) at reflux for 15 minutes gave tetramethyl dichloropyromellitate, m.p. 175-177° (from acetone), undepressed on admixture with authentic ester and having an identical infra-red spectrum.

(8) Attempted Fluorination of Dichloropyromellitoyl Chloride The acid chloride (1.83g., 0.005 mole) and dry potassium fluoride (4g., 0.069 mole) were heated in an autoclave under nitrogen to 250° in 4.5 hours and kept at 250° a

further 4 hours. A 25% increase in cold pressure was noted. Continuous benzene extraction of the product for 20 hours and evaporation of the solvent gave a red gum (0.42g.) which, when recrystallised from toluene, yielded a brown powder (0.1g.). It dissolved in hot water to form an acid solution free of chloride ion. A fluoride ion test was inconclusive. Evaporation of the toluene mother liquor gave a viscous red gum with the same qualitative composition. Sodium fusion of both materials gave solutions containing chloride ion.

c. Preparation via p-Difluorotetracyanobenzene

(1) p-Difluorotetrabromobenzene To bromine (1122g., 374 ml., 7.0 mole) cooled to 0° was slowly added aluminum (2.5g.) in small pieces. Then the temperature was allowed to rise to 20° and p-difluorobenzene (100g., 0.88 mole) run in over 1 hour, the temperature being kept at 20° or below. The mixture was kept at room temperature overnight, then heated at 50°-60° for four hours. The mixture was poured onto crushed ice, the solid collected, washed with water, potassium bisulphite solution, sodium carbonate solution and finally with water again. Crude yield 366g., (97%), m.p. 161-165°. A sample was twice recrystallised from benzene/petrol ether to give white crystals of p-difluorotetrabromobenzene, m.p. 164.5°-166°.

Anal. Calc'd. for  $C_6Br_4F_2$ : C, 16.8; Br, 74.4; F, 8.8%

Found: C, 16.9; Br, 74.1; F, 8.1

(2) Reaction of p-Difluorotetrabromobenzene with Cuprous Cyanide in Dimethylformamide Para-difluorotetrabromobenzene (107g., 0.25 mole), cuprous cyanide (100.8g., 1.12 mole) and dry dimethylformamide (250 ml.) were stirred and heated to reflux temperature in 35 minutes and held at reflux a further 2.5 hours. The initial light green colour had by then darkened to green-black. The hot mixture was poured into a solution of ferric chloride (300g.) in 3.5N hydrochloric acid (770 ml.), the resultant mixture was stirred and heated at 80-90° for 1 hour and allowed to cool overnight. The black solid obtained was boiled with water to remove inorganic material, collected and dried over phosphoric oxide. It weighed 83g.

No sublimation of this supposed crude tetranitrile occurred at 220°/0.35 mm. and continuous ether extraction of 10g. yielded a black tar (2.9g.) which could not be crystallised. Hydrolysis of the crude material was then attempted.

(3) Hydrolysis of p-Difluorotetracyanobenzene (?) To the crude material (50g.) from the previous experiment was added

conc. sulphuric acid (100 ml.) over 10 minutes. The mixture was stirred at 80-100° for one hour, then the temperature was raised to 120°, conc. nitric acid (20 ml.) added over 25 minutes and the mixture heated at 120-150° for a further 1.5 hours. When it was cool, water (100 ml.) was slowly added and the mixture refluxed for 2 hours, then diluted with water (600 ml.). Continuous ether extraction of this solution for 32 hours and evaporation of the extracts gave an orange solid (17.2g.), m.p. 202-220°. After a sodium fusion, positive tests for nitrogen and fluorine were obtained. A test for bromine was negative. The product dissolved in water to give an acid solution. Infra-red spectrum showed the presence of carboxyl and the absence of nitrile absorptions, while amide or imide absorptions if present were obscured by those due to hydroxyl groups. (I.R. Spectrum No. 3209).

Attempts to recrystallise this material were unsuccessful and sublimation at 150°/0.15 mm. gave only a small amount of sublimate with a wide melting range (200-210°), possibly crude difluoropyromellitic acid.

The material was treated with nitrous acid to convert any remaining amide groups to carboxyl.

(4) Action of Nitrous Acid on the Crude Acid To a stirred mixture of the crude acid (14.5g.) in 60% sulphuric acid (130 ml.) was added over 15 minutes a solution of sodium nitrite (14g.) in 15 ml. water while the temperature was kept at 20-30°. The solution was heated at 80° until gas evolution ceased (1 hour), diluted with water to 700 ml. and continuously ether extracted for 30 hours. Evaporation of the dried extracts yielded a hygroscopic, yellow solid (12.7g.). (I.R. No. 3362). This spectrum is similar to that (I.R. No. 3351) of difluoropyromellitic acid obtained by oxidation of difluorodurene. By sodium fusion this solid was shown to contain fluorine but not nitrogen or bromine. Again, recrystallisation was not successful.

(5) Methylation of the Crude Acid A cold solution of diazomethane (5.9-6.1g.) in ether (500 ml.) was added portionwise over 30 minutes to the acid (8.81g.) suspended in ether (300 ml.) while the temperature was kept at -20° to -12°. Excess diazomethane was present at the end of the addition and a clear solution remained. Evaporation of the ether gave a tacky brown mixture of liquid and crystals (9.99g.) which was washed with acetone to give a solid residue (3.73g.). Two recrystallisations from benzotrifluoride yielded pale yellow crystals (0.53g.), m.p. 115-118°. The infra-red spectrum (I.R. No. 3282) shows the presence of methyl groups and ester carbonyl absorptions and is practically identical to the spectrum (I.R. No. 3376) of the



ester formed by methylation of the acid derived from the oxidation of difluorodurene.

Anal. Calc'd. for  $C_{14}H_{12}F_2O_8$ : C, 48.55; H, 3.5; F, 11.0%

Found: C, 48.7; H, 3.60; F, 11.5

### 3. TETRAFLUORO-META-PHENYLENEDIAMINE

#### a. Ammination of Pentafluoroaniline

(1) 210° for 30 hours Pentafluoroaniline (20g., 0.11 mole) and ammonia (20 ml., s.g. 0.880, 60% excess) were sealed in a glass ampoule and shaken at 210° for 30 hours. Crude liquid and solid product (38g.) was removed and steam distilled. The cooled distillate was filtered to give crystalline product which weighed 13g. after drying in vacuo. Recrystallisation from 80°-100° petrol ether gave 7.4g. (82% m- $C_6F_4(NH_2)_2$  by gas chromatography.)

(2) 205° for 60 hours Pentafluoroaniline (341g., 1.86 mole) and ammonia (330 ml., s.g. 0.880, 100g.) were stirred in an autoclave at 205° for 60 hours. Treatment of the crude product (196g.) as in (1) above gave tetrafluoro-m-phenylenediamine (166g.), m.p. 127-129°. (89% m- $C_6F_4(NH_2)_2$ , 9.5% p- $C_6F_4(NH_2)_2$  by gas chromatography on a Versamid column.)

#### b. From 1,2,3,5-Tetrafluorobenzene by Nitration and Reduction

(1) 2,3,4,6-Tetrafluoronitrobenzene 1,2,3,5-Tetrafluorobenzene (50g., 0.33 mole) and concentrated sulphuric acid (60 ml.) were cooled to approx. 0° and a mixture of concentrated nitric acid (24 ml.) and concentrated sulphuric acid (20 ml.) slowly added over 1/2 hour so that the temperature remained at 0°. The mixture was stirred at this temperature for 3 1/2 hours, poured onto ice (400g.) and the organic material separated, washed (3 x 250 ml. water) and dried. Yield 49.1g., 78% pure by gas chromatography.

#### (2) Attempted Nitration of 2,3,4,6-Tetrafluoronitrobenzene

(a) With Fuming Nitric and Concentrated Sulphuric Acids  
To a stirred mixture of concentrated sulphuric acid (24 ml.) and fuming nitric acid (19 ml., s.g. 1.5) was added 2,3,4,6-tetrafluoronitrobenzene (28.2g., 0.15 mole) over 10 minutes and the mixture was then heated at 100° for 2 hours. The product was poured onto crushed ice and the organic layer separated (22.9g.)

and shown by gas chromatography to contain starting material (94.7%) and several other unidentified components.

(b) With Cupric Nitrate in Acetic Anhydride 2,3,4,6-Tetrafluoronitrobenzene (19.5g., 0.1 mole), 36.2g. of cupric nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) and 70 ml. of acetic anhydride were stirred at room temperature with little apparent reaction. When warmed to  $50^\circ$  a vigorous reaction ensued which was controlled by cooling. The mixture was then heated at  $50-60^\circ$  for 1 hour and poured into water (500 ml.). Sulphuric acid (18N, 50 ml.) was added and the organic layer separated. It was 89% starting material by gas chromatography and 11% of unidentified more volatile materials.

(3) 2,3,4,6-Tetrafluoroaniline To a stirred mixture of iron filings (70g., 1.25g. atom) and ammonium chloride solution (90 ml., 0.08N) was added approx. 5 ml. of 2,3,4,6-tetrafluoronitrobenzene, causing a small rise in temperature. The mixture was then heated to  $50^\circ$  and drop-wise addition of the nitro-compound continued causing a rapid rise to reflux temperature. Addition continued at a rate sufficient to maintain reflux and was complete in 45 minutes. The total amount added was 72g., 0.37 mole. The solution was held at gentle reflux for 2 1/2 hours and steam distilled to yield 2,3,4,6-tetrafluoroaniline (51.6g., 85% yield), 99% pure by gas chromatography (I.R. No. 3782).

(4) 2,3,4,6-Tetrafluoroacetanilide 2,3,4,6-Tetrafluoroaniline (43.8g., 0.27 mole) was added to a mixture of acetic anhydride (40 ml.), glacial acetic acid (40 ml.) and zinc dust (0.2g.) and the mixture refluxed for 1/2 hour. Addition of the resultant solution to ice water (1 liter) yielded a white precipitate, which was collected, washed with 5% bicarbonate solution and dried (phosphoric oxide). Crude yield: 49.5g., m.p.  $120-140^\circ$ . Recrystallisation from aqueous ethanol gave 2,3,4,6-tetrafluoroacetanilide (43.2g., 77% yield), m.p.  $141-142.5^\circ$  (Finger et al. cite  $140-1^\circ$  ref. 9). (I.R. No. 3390).

Anal. Calc'd. for  $\text{C}_8\text{H}_5\text{F}_4\text{NO}$ : C, 46.4; H, 2.4; F, 36.7%

Found: C, 46.7; H, 2.6; F, 36.5

(5) Attempted Nitration of 2,3,4,6-Tetrafluoroacetanilide 2,3,4,6-Tetrafluoroacetanilide (5g., 0.024 mole) was added in portions over 10 minutes to stirred concentrated sulphuric acid at  $0-5^\circ$  and the temperature maintained at  $5-10^\circ$  while concentrated nitric acid was added over 30 minutes. Stirring was continued at  $10-15^\circ$  for 3 1/2 hours, and the orange solution then poured onto crushed ice (300g.). The solid product was filtered off,

washed and dried (phosphoric oxide). Yield: 3.98g., m.p. 140-143°, undepressed on admixture with authentic 2,3,4,6-tetrafluoroacetanilide and having an identical infra-red spectrum.

c. Preparation by Hydrogenation and Dehydrofluorination of 1-Amino-3-imino-2,4,4,5,5,6,6-heptafluorocyclohexene

15g. of 1-Amino-3-imino-2,4,4,5,5,6,6-heptafluorocyclohexene (Technical Documentary Report No. ML-TDR 64-89) dissolved in ethanol (250 ml.) was hydrogenated at 30-50° and atmospheric pressure in the presence of Raney nickel (18g.) and Amberlite IRA 400 (OH) resin (12g.). When absorption of hydrogen had ceased the solvent was removed and the residue crystallised from 40% ethanol to yield 1.4g. (14%). Recrystallisation from 60% acetic acid followed by sublimation gave tetrafluoro-m-phenylenediamine, m.p. 131.5-133°, 98.2% purity by gas chromatography (Versamid column).

4. TETRAFLUORO-o-PHENYLENEDIAMINE

a. 2,3,4,5-Tetrafluoronitrobenzene

A nitrating mixture consisting of concentrated nitric acid (600 ml.) and concentrated sulphuric acid (900 ml.) was added during 1 1/2 hours to stirred 1,2,3,4-tetrafluorobenzene (512g., 2.62 mole) maintained at 25-30°. After stirring the mixture for 1 hour, it was poured onto ice (2000g.). The organic layer was washed with water, dried (CaCl<sub>2</sub>) and distilled yielding 2,3,4,5-tetrafluoronitrobenzene (450g., 64% yield), b.p. 76-79°/-16 mm., a yellow, lachrymatory liquid. Gas chromatography on a silicone oil/celite column at 150° showed that this product was 96% purity. I.R. Spectrum No. 2266.

Anal. Calc'd. for C<sub>6</sub>HF<sub>4</sub>NO<sub>2</sub>: C, 36.9; H, 0.6; F, 39.0%

Found: C, 36.9; H, 0.7; F, 38.4

b. 2,3,4,5-Tetrafluoroaniline

Concentrated hydrochloric acid (835 ml.) was added during 1.5 hours to a stirred mixture of granulated tin (450g.) and 2,3,4,5-tetrafluoronitrobenzene (400g., 2.05 mole). The mixture was heated on a steam bath for 1 hour, cooled, neutralised (Na<sub>2</sub>CO<sub>3</sub>) and steam distilled. There was obtained 2,3,4,5-tetrafluoroaniline (263g., 78% yield), a colourless liquid which crystallised at 20°. This product was 99% pure by gas chromatography on a silicone oil/celite column at 150°, I.R. Spectrum No. 2453.

c. 2,3,4,5-Tetrafluoroacetanilide

2,3,4,5-Tetrafluoroaniline (50g., 0.30 mole), acetic anhydride (125 ml.) and sulphuric acid (1 drop) were allowed to react at normal temperature for 2 days. The mixture was then poured into cold water (1 liter). The white solid was filtered off and washed with sodium carbonate solution and with water yielding 2,3,4,5-tetrafluoroacetanilide (56.7g., 90% yield), m.p. 103.5-105.5°.

A preliminary preparation gave a yield of 91%, m.p. 106-107.5°.

Anal. Calc'd. for  $C_8H_5F_4NO$ : C, 46.4; H, 2.4; F, 36.7%

Found: C, 46.5; H, 2.5; F, 36.2

d. 2-Nitro-3,4,5,6-Tetrafluoroacetanilide

2,3,4,5-Tetrafluoroacetanilide (50g., 0.24 mole) was added to sulphuric acid (150 ml.) keeping the temperature below 15°. Nitric acid (140 ml.) was added dropwise to the cooled mixture, keeping the reaction temperature at 10-15°. When the addition was complete (1 hour), the mixture was stirred at 10-15° for a further 2 hours, then poured onto ice. The yellow solid was filtered off, washed and dried giving 2-nitro-3,4,5,6-tetrafluoroacetanilide (48g., 79% yield), m.p. 143-147.5°.

Preliminary experiments gave a product m.p. 149-152.5° after crystallisation from ethanol/water.

Anal. Calc'd. for  $C_8F_4H_4N_2O_3$ : C, 38.1; H, 1.6; F, 30.1%

Found: C, 37.8; H, 2.0; F, 29.6

e. 2-Nitro-3,4,5,6-Tetrafluoroaniline

2-Nitro-3,4,5,6-tetrafluoroacetanilide (46.5g., 0.185 mole) and 50% w/w sulphuric acid (200 ml.) were refluxed for 2 hours. After cooling, the product was filtered off and washed. The aqueous filtrate was extracted with ether (2 x 100 ml.). The solid was dissolved in the ether extract and the ether was removed leaving crude 2-nitro-3,4,5,6-tetrafluoroaniline (22.7g.). This was sublimed giving a deep red solid (40% yield), m.p. 42-43.5°, I.R. Spectrum No. 2741. Brooke et al. (ref. 20) cited m.p. 42.5-43.5°.

Anal. Calc'd. for  $C_6H_2F_4N_2O_2$ : C, 34.3; H, 0.95; F, 36.2%

Found: C, 33.9; H, 1.3; F, 35.4

f. 3,4,5,6-Tetrafluoro-o-phenylenediamine

2-Nitro-3,4,5,6-tetrafluoroaniline (10.5g., 0.05 mole) dissolved in ethanol (100 c.c.) was hydrogenated at room temperature and atmospheric pressure, using Raney nickel (1g.) as catalyst. The hydrogenation had practically stopped after 3.5l. of hydrogen had been absorbed. The nickel was filtered off and the filtrate concentrated to 30 c.c. and poured into water. The brown solid was filtered off, dried and sublimed at 100°/0.5 mm. yielding 3,4,5,6-tetrafluoro-o-phenylenediamine (6.7g., 74.5% yield). Recrystallisation from benzene gave m.p. 127.5-129.5°. Brooke et al. cited m.p. 131-131.5° (ref. 20). I.R. Spectrum No. 2901 showed the presence of NH<sub>2</sub> and fluorinated aromatic ring.

Anal. Calc'd for C<sub>6</sub>H<sub>4</sub>F<sub>4</sub>N<sub>2</sub>: C, 40.0; H, 2.2; F, 42.3%

Found: C, 39.9; H, 2.4; F, 41.9

5. TETRAFLUORO-p-PHENYLENEDIAMINE

a. 4-Aminotetrafluorobenzonitrile

Pentafluorobenzonitrile (100g.) and ammonium hydroxide (100 ml., s.g. 0.880) were stirred at ambient temperature for 6 hours and then kept for 60 hours. The solid product (100g.), m.p. 76-84°, was recrystallised from aqueous ethanol to give 4-aminotetrafluorobenzonitrile (81%), 79.4g., m.p. 94-96° (I. R. No. 2917).

b. 4-Aminotetrafluorobenzamide

4-Aminotetrafluorobenzonitrile (25g.) and concentrated sulphuric acid (100g.) were stirred together, heated to 80° over 15 minutes, maintained at that temperature for 1 hour, cooled and poured onto crushed ice. The precipitated product was collected and washed with ice-water. Recrystallisation from water gave a first crop (22g.), m.p. 188-189.5°, and a second crop (1.8g.) m.p. 187-189.5° was obtained by cooling the mother liquor. Yield 87%.

Anal. Calc'd. for C<sub>7</sub>H<sub>4</sub>F<sub>4</sub>N<sub>2</sub>O: C, 40.4; H, 1.9%

Found: C, 40.6; H, 2.2

c. Tetrafluoro-p-phenylenediamine

To a solution of sodium hydroxide (12g.) in water (150 ml.), cooled to 0° was added bromine (9.5g.) followed by p-aminotetrafluorobenzamide (10.4g.). The solution was stirred at 0° for 1 hour, then heated on a steam bath for 4 hours. Ether extraction (3 x 75 ml.) and evaporation of the dried extracts gave yellow solid (2.0g.). Sublimation at 100° and 0.5 mm. gave pale lemon needles (1.3g., 14.5%), m.p. 145.5-146.5°.

Anal. Calc'd. for  $C_6H_4F_4N_2$ : C, 40.4; H, 2.2; N, 15.6%

Found: C, 39.9; H, 2.4; N, 15.6

(I.R. Spectrum No. 3138)

6. 3,4,3',4'-TETRAMINOHEXAFLUOROBIPHENYL

a. 4,4'-Dinitro-octafluorobiphenyl

To a stirred mixture of trifluoroacetic anhydride (25 ml.), chloroform (25 ml.) and 82% hydrogen peroxide (10g.) was added 4,4'-diamino-octafluorobiphenyl (9g., 27.4 m. mole) in small portions with cooling. The solution became a yellow brown colour after each addition and the next portion was not added until it had turned apple green. A further quantity (30 ml.) of chloroform was added during the reaction. The mixture was refluxed for 45 minutes, when it turned yellow. Hydrogen peroxide (5 ml.) and chloroform (10 ml.) were added and the mixture refluxed for 75 minutes longer. It was cooled, 50 ml. of water added, the organic layer was separated, washed with water and dried. The solid (10.2g.) obtained on evaporating the chloroform was recrystallised from ether/40-60° petrol ether giving 4,4'-dinitro-octafluorobiphenyl (5.9g., 55% yield), m.p. 86-88°, I.R. Spectrum No. 2745.

Anal. Calc'd. for  $C_{12}F_8N_2O_4$ : C, 37.1; F, 39.2; N, 7.2%

Found: C, 37.0; F, 38.6; N, 6.9

In a second experiment using 144g. of 4,4'-diamino-octafluorobiphenyl the yield of 4,4'-dinitro-octafluorobiphenyl was 118g., 69%.

An improved procedure is as follows: Trifluoroacetic acid was prepared as described above from 82% hydrogen peroxide (240 ml.) and trifluoroacetic anhydride (950 ml.) at 0°. Washed,

dried chloroform (600 ml.) was added and the mixture allowed to warm to room temperature. A portion (ca. 1g.) of 4,4'-diamino-octafluorobiphenyl was added and the mixture warmed until the solvent refluxed. Diaminooctafluorobiphenyl (232g.) was added portionwise over 1 hour, keeping the mixture at gentle reflux. Hydrogen peroxide (15 ml.) was added and the mixture was refluxed for 1 hour. Water (1300 ml.) was added and the organic layer separated, water washed and dried. The solvent was removed, leaving a yellow solid (253.6g.). Distillation gave 192.9g. of crude 4,4'-dinitrooctafluorobiphenyl, b.p. 168-170°/0.25 mm. Recrystallisation from methanol gave 164.6g. (60% yield), m.p. 85-87°. A small portion (10g.) was recrystallised from (1) petroleum ether, b.p. 60-80°, (2) methanol, giving white needles, m.p. 88-89°.

b. 3,3'-Diamino-4,4'-dinitrohexafluorobiphenyl

Ammonia was bubbled into a solution of 4,4'-dinitrooctafluorobiphenyl (9.7g.) in dry ether (100 ml.) for 6 hours, then the mixture was kept at 20° for 60 hours. Ammonium fluoride was filtered off and evaporation to dryness of the filtrate gave a dark red solid. Recrystallisation from ethanol gave dark red needles (3.2g.) of 3,3'-diamino-4,4'-dinitrohexafluorobiphenyl m.p. 210-211°, (I.R. No. 2907), and a second crop (2.5g.) m.p. 206-207°.

Anal. Calc'd. for  $C_{12}H_4F_6N_4O_4$ : C, 37.7; H, 1.0; F, 29.8%

Found: C, 38.1; H, 1.8; F, 28.9

A reaction using 97g. of 4,4'-dinitro-compound gave 77g. (80%) of product, m.p. 206-209°.

An alternative procedure uses ammonium hydroxide and ether as solvent. Ammonium hydroxide (7.0 ml., s.g. 0.880, 10% excess) was stirred for 1 1/2 hours with a solution of dinitrooctafluorobiphenyl (9.4g.) in ether (60 ml.). Water (60 ml.) was then added and the ether layer was separated, washed with water, and dried. Evaporation of the ether left the crude diamine (9.9g.), m.p. 143-153°. Recrystallisation from ethanol raised the melting point to 174-178° (cf pure compound, m.p. 211-212°).

Another procedure uses ammonium hydroxide and dioxan as solvent. Ammonium hydroxide (6.5 ml., s.g. 0.880, 5% excess) was stirred for 1 1/2 hours with a solution of dinitrooctafluorobiphenyl (9.9g.) in dioxan (30 ml.). The mixture was then poured into water and the resulting red precipitate (9.1g., m.p. 197-200°) was recrystallised from xylene (50 ml.) giving 6.7g. (73%) of the diamine, m.p. 205-207°. Two more recrystallisations raised the melting point to 211 to 212°.

c. 3,4,3',4'-Tetraminohexafluorobiphenyl

A solution of 3,3'-diamino-4,4'-dinitrohexafluorobiphenyl (5g.) in ethyl acetate (25 ml.), containing Raney nickel (approx. 1g., W2 grade), was shaken under hydrogen at atmospheric pressure, 1.84 liter being absorbed in 2 hours. A colour change from orange red to brown occurred. The filtered solution was evaporated to dryness and the residue sublimed at 200° to give a small amount of crystals, m.p. 235°. The infra-red spectrum (I.R. Spectrum No. 3040) showed absence of -NO<sub>2</sub> groups.

Anal. Calc'd. for C<sub>12</sub>H<sub>8</sub>F<sub>6</sub>N<sub>4</sub>: C, 44.7; H, 2.5%

Found: C, 44.6; H, 2.6

In a second larger-scale experiment diaminodinitrohexafluorobiphenyl (75g.) yielded 41g. (59%) of crude reduction product which was recrystallised from xylene. The recrystallised material (36g.) was further recrystallised from aqueous methanol with the addition of decolourising charcoal (3g.) to give two batches of material:-

(1) 20.9g., m.p. 241-242.5°

(2) 10.6g., m.p. 238-240° (by concentrating the mother liquor)

Recrystallisation of batch (2) from aqueous ethanol in the presence of charcoal gave 6.2g., m.p. 241-242.5°. Thus the total amount of material of m.p. 241-242.5° is 27.1g. (39% yield).

d. 6,6'-Bis(2,3-diphenyl-5,7,8-trifluoroquinoxalyl)

Solutions of 3,3',4,4'-tetraminohexafluorobiphenyl (0.8g.) in acetic acid (8 ml.) and benzil (1.09g.) in acetic acid (8 ml.) were mixed and heated under reflux for 5 minutes. After cooling, the product was collected. Yield: 1.3g. Recrystallisation from acetic acid gave the bis(quinoxalyl), m.p. 274-276°, I. R. Spectrum No. 3264.

Anal. Calc'd. for C<sub>40</sub>H<sub>20</sub>F<sub>6</sub>N<sub>4</sub>: C, 71.6; H, 2.9; F, 17.0%

Found: C, 71.2; H, 3.3; F, 17.4

The preparation was repeated on twice the scale, giving 3.2g., (96.5%), m.p. 273.5-275°.



e. 3,4,3',4'-Tetra(trifluoroacetamido)hexafluorobiphenyl

3,4,3',3'-Tetraminohexafluorobiphenyl (2.0g.), trifluoroacetic anhydride (12.0 ml.) and concentrated sulphuric acid (1 drop) were refluxed for 4 hours. Carbon tetrachloride (25 ml.) was added and the volatile materials distilled off leaving a residue which was added to water (100 ml.). The solution was refluxed for 10 minutes, cooled, and the product filtered off (4.2g., 95% yield). Recrystallisation from aqueous ethanol gave 3,4,3',4'-tetra(trifluoroacetamido)hexafluorobiphenyl (1.8g.), m.p. 320° (I.R. No. 3784).

Anal. Calc'd. for  $C_{20}H_4F_{18}N_4O_4$ : C, 34.0; H, 0.6; F, 48.5%

Found: C, 34.2; H, 0.8; F, 47.7

7. 3,3'-DISUBSTITUTED-4,4'-DINITROHEXAFLUOROBIPHENYLS

a. 3,3'-Dihydroxy-4,4'-dinitrohexafluorobiphenyl

A solution of sodium hydroxide (5.0g.) in 10 ml. water was stirred with a solution of dinitrooctafluorobiphenyl (9.7g.) in dioxan (30 ml.) for 30 minutes at room temperature and then for 1 hour at 90°. The mixture was then poured into water (100 ml.) and hydrochloric acid (15 ml.) was added. The yellow oil which formed was extracted with ether (100 ml.) and the ether extract shaken with 8% sodium hydroxide (1 x 50 ml. and 2 x 25 ml.). The alkaline extract was acidified with conc. hydrochloric acid (2.5 ml.) and extracted with chloroform. Removal of the chloroform yielded a residue which was recrystallised from aqueous methanol to give yellow crystals (1.3g.), m.p. 144-145°. (I.R. Spectrum No. 3271).

Anal. Calc'd. for  $C_{12}H_2F_6N_2O_6$ : C, 37.5; H, 0.5; F, 29.6%

Found: C, 37.3, 37.4; H, 0.9, 1.1;  
F, 29.6

Powdered potassium hydroxide (10.0g.) was added quickly to a solution of dinitrooctafluorobiphenyl (9.7g.) in tertiary butanol (50 ml.) at 70°. The temperature of the mixture rose to 80°. After 30 minutes stirring at 60-70°, the mixture was cooled to room temperature and treated with water (100 ml.) and hydrochloric acid (25 ml.). Butanol was distilled off, the residue was cooled, and the solid (11.5g.) was collected. Recrystallisation from petroleum ether (b.p. 80-100°) gave orange dihydroxydinitrohexafluorobiphenyl (6.7g.), m.p. 148-150°.

The above experiment was repeated using potassium hydroxide (80g.), t-butanol (380 ml.) and dinitrooctafluorobiphenyl (75g.). The yield of dihydroxy- compound was 69.9g., (94%), m.p. 145-151°. Recrystallisation gave 45.6g. (61%), m.p. 148-150°.

b. 3,3'-Dimercapto-4,4'-dinitrohexafluorobiphenyl

A solution of sodium ethoxide prepared from sodium (1.23g.) and ethanol (30 ml.) was saturated with hydrogen sulphide. The sodium hydrosulphide solution so obtained was added at 0° to a stirred solution of 4,4'-dinitrooctafluorobiphenyl (10.25g.) in dioxan at 0° and stirring continued at 0° for 30 minutes then at 10° for a further 30 minutes. Glacial acetic acid (6 ml.), then water (150 ml.) were added. The precipitated yellow solid was dissolved in methylene chloride (110 ml.), the solution dried, and evaporated to give a yellow solid, melting range 110-170° (decomp.).

Anal. Calc'd. for  $C_{12}H_2F_6N_2O_4S_2$ : C, 34.6; H, 0.5; F, 27.5%

Found: C, 39.5; H, 1.0; F, 29.1

c. 3,3'-Dihydroxy-4,4'-diaminohexafluorobiphenyl

3,3'-Dihydroxy-4,4'-dinitrohexafluorobiphenyl (6.0g.), dissolved in methylated spirits (60 ml.), was hydrogenated at 25-40° in the presence of Raney nickel (3g.) until uptake of hydrogen was complete (45 minutes). The catalyst was filtered off and the solvent evaporated leaving a residue which was recrystallised from water yielding pale brown needles, m.p. 190.5-191.5°.

Repetition of the process using 3,3'-dihydroxy-4,4'-dinitrohexafluorobiphenyl (38.8g.), Raney nickel (15g.) and ethanol (400 ml.) gave the diamine (20.5g., 63%), m.p. 191-192°.

Anal. Calc'd. for  $C_{12}H_6F_6N_2$ : C, 44.5; H, 1.9; F, 35.2%

Found: C, 44.6; H, 2.0; F, 34.5

(I.R. No. 3334)

8. DECAFLUORODIPHENYLAMINE

Sodium hydride (25g., 50% in oil) was added to a solution of pentafluoroaniline (90g.) in dry dioxan (1 liter) and the mixture was heated under reflux for 30 minutes. Hexafluorobenzene (100g.) was then added and the mixture was heated under

reflux for 4 hours, then poured into water (3l.) and hydrochloric acid (250 ml.). Extraction with methylene chloride (1 x 50 ml., 1 x 100 ml.) and distillation of the dried extract gave:-

pentafluoroaniline, b.p. 62-110°/31 mm., 18.9g.

decafluorodiphenylamine, b.p. 145-146°/31 mm., m.p. 83.5-84.5°, 69.1g. (40%). I.R. Spectrum No. 3208.

Anal. Calc'd. for  $C_{12}HF_{10}N$ : C, 41.3; H, 0.3; F, 54.4%

Found: C, 41.5; H, 0.4; F, 53.9

This preparation was repeated yielding decafluorodiphenylamine in 59% yield (39% conv.), m.p. 85-86.5°. Burdon et al. cited m.p. 85-87° (ref. 11).

The N-acetyl derivative, m.p. 122-124°, was prepared in the usual way.

Anal. Calc'd. for  $C_{14}H_3F_{10}NO$ : C, 43.0; H, 0.8; F, 48.6%

Found: C, 42.8; H, 1.0; F, 48.1

## 9. 1,4-BIS(PENTAFLUOROANILINO)TETRAFLUOROBENZENE

### a. At 170°

Pentafluoroaniline (18g.), decafluorodiphenylamine (36.9g.), sodium hydride (5.0g.), and dioxan (330 ml.) were heated for 6 hours at 170° in an autoclave, then the mixture was diluted with water (1400 ml.) and extracted with methylene chloride (1 x 200 ml., 1 x 100 ml.). The solvent was distilled from the dried extract. Distillation of the residue gave:-

decafluorodiphenylamine, 22.5g., b.p. 100-110°/1 mm.

a small high-boiling fraction which sublimed.

The fraction above was re-sublimed at 100-150°/0.03 mm. and the sublimate (0.8g.), m.p. 158-169° was recrystallised from petroleum ether (b.p. 80-100°) giving 1,4-bis(pentafluoroanilino)tetrafluorobenzene (0.4g.), m.p. 177-179°.

Anal. Calc'd. for  $C_{18}H_2F_{14}N_2$ : C, 42.2; H, 0.4; F, 52.0%

Found: C, 42.2; H, 0.8; F, 50.8

Infra-red spectrum No. 3266 had an absorption band at  $3330\text{ cm}^{-1}$  (NH).

b. At  $220^\circ$

Pentafluoroaniline (18g.), decafluorodiphenylamine (36.9g.), sodium hydride (5.0g., 50% dispersion in oil) and dioxan (300 ml.) were heated in a nitrogen filled autoclave at  $220^\circ$  for 4 1/2 hours. The mixture was diluted to 1500 ml. and acidified with glacial acetic acid (10 ml.). The organic layer was extracted with methylene chloride, the extract dried, the solvent removed, and the residue distilled yielding:-

a fraction (29.4g.), b.p.  $120-140^\circ/20\text{ mm.}$  Two recrystallisations from petrol ether (b.p.  $80-100^\circ$ ) gave decafluorodiphenylamine (16.2g.), m.p.  $84-86^\circ$ .

a dark purple residue, which was sublimed from a bath at  $80-90^\circ$  to give 2.7g. of decafluorodiphenylamine. Further sublimation of the residue at a bath temperature of  $130-140^\circ$  gave 1.4g. of crude 1,4-bis(pentafluoroanilino)tetrafluorobenzene, which was recrystallised from petroleum ether (b.p.  $80-100^\circ$ ) giving the pure compound (0.7g.), m.p.  $177.5-179.5^\circ$ .

#### 10. OCTAFLUORONAPHTHALENE

Tetramethylene sulphone (6.5 kg.), potassium fluoride (2.5 kg.) and benzene (500 ml.) were azeotroped to remove water and the mixture was then heated to a pot temperature of  $220^\circ$  to remove benzene. Octachloronaphthalene (147g., "Hallowax 1051") was then added and the mixture stirred at  $235^\circ$  for 14 hours. Crude octafluoronaphthalene was distilled from the mixture at  $180-200^\circ/40\text{ mm.}$  The solidified material was melted and poured into water to remove tetramethylene sulphone, then redistilled. The distillate, b.p.  $148-150^\circ/119\text{ mm.}$ , was recrystallised from ethanol and redistilled giving octafluoronaphthalene, b.p.  $204-208^\circ/760\text{ mm.}$ , (454g., 50% yield). (I.R. No. 3397).

## 11. TETRAFLUORORESORCINOL

### a. Attempted Preparations of Phenols by Hydrolysis of Fluoro-aryl Sulphates and Sulphonates

The feasibility of this type of reaction was tested by attempting to replace the iodine atom in iodopentafluorobenzene with a group which could be hydrolysed, thus giving pentafluorophenol.

(1) Using Chloro- or Fluoro-sulphonic Acid Neither chlorosulphonic acid nor fluorosulphonic acid when heated under pressure with iodopentafluorobenzene at temperatures from 140° to 190° yielded any of the desired halosulphate.

(2) Using Toluene-p-sulphonic Acid No reaction occurred when iodopentafluorobenzene was heated with silver toluene-p-sulphonate in acetonitrile, or in dimethylformamide, for prolonged periods.

### b. Attempted Preparation by Substitution of Bromine Atoms by Hydroxyl Groups in Polyfluoroaryl Bromides

Trial reactions involved the preparation of pentafluorophenol from bromopentafluorobenzene.

Bromopentafluorobenzene was heated with an aqueous suspension of potassium fluoride and cuprous oxide or silver oxide at temperatures from 195° to 250° for periods of from 5 to 65 hours. Pentafluorophenol was obtained in yields of 2-15% together with pentafluorobenzene in approximately 5% yield. A similar reaction with 1,3-dibromotetrafluorobenzene yielded mainly a polymeric material, together with small amounts of reduction products.

### c. Substitution of Fluorine by Hydroxyl in Pentafluorophenol

(1) Using Potassium Hydroxide in Tertiary Butanol A mixture of potassium pentafluorophenate (22.2g., 0.10 mole), powdered potassium hydroxide (13.2g., 85% KOH, 0.20 mole), and t-butanol (200 ml.) were stirred and heated at reflux temperature for 33 hours. Water (300 ml.) was added, the t-butanol distilled off at 20 mm., and more water (250 ml.) added. On acidification, a small quantity of yellow oil separated. Extraction with methylene chloride (50 ml.) and evaporation of the solvent gave a liquid residue (15.3g.). Gas chromatography showed that this contained only methylene chloride (39%) and pentafluorophenol (61%). Exhaustive ether extraction of the aqueous phase gave a viscous, yellow liquid (6.5g.), which appeared to be wet. It was

dissolved in benzene (10 ml.), the solution filtered, the benzene was distilled off and the remaining liquid was distilled giving:-

- (a) 2.5g., b.p. 90-150°
- (b) 0.1g., b.p. 80-120°/10 mm.

Gas chromatography showed that fraction (a) contained benzene (21%) and pentafluorophenol (61%), and fraction (b) contained pentafluorophenol (86%). Both fractions contained numerous other small peaks, none of which had the retention time for tetrafluoro-resorcinol. The recovery of pentafluorophenol is 11.5g. (cf. 18.4g.  $C_6F_5OH$  taken for this experiment as the potassium salt).

(2) Using Potassium Hydroxide in Water A mixture of 85% flake potassium hydroxide (201g., 3.05 mole), distilled water (387 ml.) and hexafluorobenzene (186g., 1.0 mole) was heated at 150° for 6 hours in a stainless steel rocking autoclave. The cooled mixture was added to water and the organic layer (129.5g.) separated. This was unchanged hexafluorobenzene, b.p. 79-80°. The aqueous layer was acidified and extracted with methylene chloride (5 x 150 ml.). This extract was distilled to leave a residue (4.4g.). Further distillation gave:-

- (a) 2.8g., b.p. 139-150°
- (b) 1.1g., b.p. 120-130°/35 mm.
- (c) a residue (0.3g.)

Fraction (a) contained  $CH_2Cl_2$  (5%) and  $C_6F_5OH$  (93%), by g.l.c. Fraction (b) solidified, m.p. 70-105°. Redistillation of a part (0.6g.) of fraction (b) gave a solid (0.2g.), b.p. 110-115°/20 mm., m.p. 93-98°. This product gave a violet colour with a neutral ferric chloride solution. Tetrafluorohydroquinone does not give a colour reaction with neutral ferric chloride solution.

A mixture of pentafluorophenol (185g., 1.0 mole), potassium hydroxide (201g. of 85% KOH, 3.05 mole), and water (500 ml.) in a 1 liter stainless steel autoclave was rocked and kept at 150° for 5 hours and the product added to hydrochloric acid (1500 ml. of 4N acid). Extraction with methylene chloride (5 x 200 ml.) and distillation of the extract gave a residue (88.5g.). Further distillation of this residue through a 4" Vigreux column gave 79g. of pentafluorophenol, b.p. 145-150°, and a brown residue A (5.9g.).

Exhaustive ether extraction of the aqueous liquors from the methylene chloride extraction afforded a liquid product (104g.) to which residue A was added. Distillation of this product gave:-

- (a) 30.0g., b.p. 20-160°, mainly ether
- (b) 11.5g., b.p. 60-124°/25 mm. (solidified in receiver)
- (c) 42.5g., b.p. 124-128°/25 mm. (solidified in receiver)
- (d) 21.0g. (boiler residue)

Fraction (b) was shown by gas chromatography to contain pentafluorophenol (75%) and tetrafluororesorcinol (24%), while fraction (c) was tetrafluororesorcinol (99+%). A part (15g.) of fraction (c) was recrystallised, twice from benzotrifluoride and once from benzene to yield white crystals of tetrafluororesorcinol (9.2g.), m.p. 88-95°.

Anal. Calc'd. for  $C_6H_2F_4O_2$ : C, 39.6; H, 1.1; F, 41.8%

Found: C, 39.2; H, 1.3; F, 41.7

The meta orientation of the hydroxyl groups was confirmed by N.M.R. spectroscopy.

Treatment of 1g. of tetrafluororesorcinol with p-toluenesulphonyl chloride (2.0g.) in pyridine (5 ml.) gave the bis(p-toluenesulphonate), (2.2g.). Recrystallisation of this derivative from ethanol gave (0.9g.), m.p. 114-115°.

Anal. Calc'd. for  $C_{20}H_{14}F_4O_6S_2$ : C, 49.0; H, 2.9%

Found: C, 49.0; H, 2.8

A similar derivative prepared from tetrafluorohydroquinone had m.p. 153-4°. Burdon et al. (ref. 14) cited m.p. 118-120° for the bis(p-toluenesulphonate) prepared from tetrafluorocatechol.

A further preparation of tetrafluororesorcinol using the conditions described in (2)(b) above gave material of 97% purity (gas chromatographic analysis) in 38% yield. Recrystallisation from dry benzene and storage of the product over phosphoric oxide at 40°-50°/0.1 mm. for 13 hours gave tetrafluororesorcinol, m.p. 94-98°. Wall cited m.p. 95-96° (ref. 13). I.R. No. 3075, 3076.

## 12. 1,4-BIS(PENTAFLUOROPHENYLTHIO)TETRAFLUOROBENZENE

1,4-Dibromotetrafluorobenzene (28.3g., 0.09 mole), cuprous pentafluorothiophenate (48.3g., 0.18 mole) and dimethylformamide (200 ml.) were stirred at 140° under nitrogen for 90 minutes,

then poured into water (1 liter). The precipitate was washed with water, dried, and ether extracted to give the crude thio-ether (55.4g.). Three recrystallisations from dimethylformamide and two from n-butanol gave 29.0g., (58%) of 1,4-bis(pentafluorophenylthio)tetrafluorobenzene, lustrous flakes, m.p. 164.5-166°. (I.R. Spectrum No. 3265).

Anal. Calc'd. for  $C_{18}F_{14}S_2$ : C, 39.6; F, 48.7%

Found: C, 40.0; F, 48.7

### 13. 1,3-BIS(PENTAFLUOROPHENYLTHIO)TETRAFLUOROBENZENE

Cuprous pentafluorothiophenate (52.5g., 0.2 mole) and 1,3-dibromotetrafluorobenzene (30.8g., 0.1 mole) were heated and stirred under nitrogen in refluxing dimethylformamide (200 ml.) for 2 hours, the initial light green colour changing to dark green. The solution was filtered and the filtrate poured into ice water (1 liter) precipitating a solid which was collected and dried in vacuo over phosphoric oxide. Exhaustive ether extraction of this material and evaporation of the dried extract gave a white solid (53g.), m.p. 114-122°. Recrystallisation from ethanol and then from ethanol/butanol gave white crystals of 1,3-bis(pentafluorophenylthio)tetrafluorobenzene (37.0g., 68% yield), m.p. 124.5-126°. (I.R. Spectrum No. 3247).

Anal. Calc'd. for  $C_{18}F_{14}S_2$ : C, 39.6; F, 48.7%

Found: C, 39.7; F, 48.2

### 14. 4,4'-BIS(PENTAFLUOROPHENYLTHIO)OCTAFLUOROBIPHENYL

4,4'-Dibromooctafluorobiphenyl (45.6g., 0.1 mole) and cuprous pentafluorothiophenate (65.6g., 0.25 mole) were stirred and heated in refluxing dimethylformamide (300 ml.) for 6 hours under nitrogen. The dark green reaction mixture was filtered, the filtrate poured into water (1.25l.), the precipitate collected, and exhaustively ether extracted. Evaporation to dryness of the extract gave a white solid (70.5g.), m.p. 154-159°. Three recrystallisations from butanol gave 4,4'-bis(pentafluorophenylthio)octafluorobiphenyl (30.8g., 44% yield), m.p. 163-166.5°. (I.R. Spectrum No. 3269).

Anal. Calc'd. for  $C_{24}F_{18}S_2$ : C, 41.5; F, 49.3%

Found: C, 41.3; F, 49.1



A further two recrystallisations from dimethylformamide gave a material (17.7g.), m.p. 164.5-166.5°.

15. TETRAFLUOROBENZENE-1,4-DITHIOL

a. 1,4-Bis(methylthio)tetrafluorobenzene

(1) From Cuprous Thiomethylate and p-Dibromotetrafluorobenzene

(a) Cuprous Thiomethylate A glass ampoule (200 ml. capacity) was packed with alternate layers of glass balls and cuprous oxide (18.9g., 0.13 mole) and cooled in solid carbon dioxide. Methanethiol (16.0g., 0.33 mole) was added by vacuum transfer, followed by cold ethanol (75 ml.). The evacuated tube was sealed, shaken, and heated at 90° for 69 hours, when a hard yellow mass containing some unreacted cuprous oxide was present. Separation of the lighter cuprous thiomethylate (17.3g., 60% yield) from the glass balls and cuprous oxide was effected by decantation in ethanol. It was a yellow solid, m.p. >310°.

Anal. Calc'd. for  $\text{CH}_3\text{CuS}$ : C, 10.9; H, 2.7; Cu, 57.5%

Found: C, 10.8; H, 2.3; Cu, 58.1

Unreacted cuprous oxide (6.5g.) was recovered.

(b) Reaction of Cuprous Thiomethylate with 1,4-Dibromotetrafluorobenzene 1,4-Dibromotetrafluorobenzene (15.39g., 0.05 mole), cuprous thiomethylate (13.80g., 0.13 mole) and dried, redistilled dimethylformamide were refluxed and stirred under nitrogen for 14 hours. The reaction mixture, consisting of a brown solid and dark green solution, was filtered and the filtrate was poured into water (100 ml.). The resulting green precipitate was collected, and exhaustively ether extracted. Evaporation of the extract gave crude 1,4-bis(methylthio)tetrafluorobenzene (9.20g., 76% yield), m.p. 54-81°, which, after two recrystallisations from methylated spirits and ethanol/benzene, was obtained as white crystals (2.39g., 20% yield), m.p. 87.5-89°.

Anal. Calc'd. for  $\text{C}_8\text{H}_6\text{F}_4\text{S}_2$ : C, 39.6; H, 2.5%

Found: C, 40.5; H, 2.2

Repetition of this preparation on the same scale gave crude and purified yields almost identical to those given above.

(2) From Sodium Thiomethylate and Hexafluorobenzene  
Methanethiol (15g., 0.31 mole) was added to dry methanol (20 ml.) at  $-50^{\circ}$  and the solution allowed to warm to  $-5^{\circ}$ . Sodium methoxide (13.5g., 0.25 mole) in methanol (35 ml.) was added in 5 minutes and the solution was allowed to warm to room temperature and finally heated to  $50^{\circ}$  to expel the excess of methanethiol. About 50 ml. of methanol was then distilled off to leave a clear, viscous solution of sodium thiomethylate in methanol.

Hexafluorobenzene (23.25g., 0.13 mole) was slowly added to the stirred sodium thiomethylate solution prepared as above. The resulting vigorous reaction was moderated by external cooling; the whole addition took 15 minutes. The mixture was refluxed for one hour, poured into water, and the white precipitate so formed collected and water washed. Yield: 17.5g., (58%), m.p.  $68-79^{\circ}$ . Three recrystallisations from  $40-60^{\circ}$  and  $60-80^{\circ}$  petrol ether gave a solid (7.3g., 24% yield), m.p.  $87-89.5^{\circ}$ , undepressed on admixture with 1,4-bis(methylthio)tetrafluorobenzene prepared from cuprous thiomethylate and 1,4-dibromotetrafluorobenzene (I.R. Spectrum No. 3292).

Repetition of this preparation using 74.4g., 0.4 mole of hexafluorobenzene and a modified procedure gave, after purification, 1,4-bis(methylthio)tetrafluorobenzene (49.3g., 51% yield), m.p.  $90.5-93^{\circ}$ .

Anal. Calc'd. for  $C_8H_6F_4S_2$ : C, 39.7; H, 2.5; F, 31.4%

Found: C, 39.5; H, 2.4; F, 31.5

b. Attempted Demethylation of 1,4-Bis(methylthio)tetrafluorobenzene

(1) With Oleum of Various Strengths and Sulphur Trioxide  
The thioether (0.02-0.03 mole) was stirred with oleum under nitrogen for periods of 2 to 24 hours and the product poured into water. With 20% oleum, 85% of starting material was recovered, while with 65% oleum only a brittle black solid, insoluble in alkali, was obtained. Using 43% oleum and stabilised sulphur trioxide very small amounts of viscous oils were obtained, shown by infra-red spectroscopy to contain some -SH and -CH<sub>3</sub> absorptions.

(2) With Hydrogen Bromide in Glacial Acetic Acid The thioether (4.92g.) was stirred with 20 ml. of a solution of 45% w/v hydrogen bromide in glacial acetic acid for 10 hours at reflux and was then poured into water. Only starting material (4.56g.) was recovered.

(3) With Sodium in Liquid Ammonia Under a nitrogen atmosphere, the thioether in liquid ammonia was treated with sodium in small portions until a permanent blue colour was obtained. The excess sodium was then destroyed by addition of solid ammonium chloride, the solution evaporated to dryness and the residue treated with alkali to take up any thiol formed. Addition of hydrochloric acid then liberated the thiol.

Three reactions were carried out using in each case 4.86g. (0.02 mole) of the thioether in 100 ml. of liquid ammonia.

With a deficiency of sodium only starting material (92%) was recovered, and with a slight excess of sodium there was obtained starting material (21%) and a viscous brown oil (1.82g.) containing, by infra-red analysis, thiol and amino groups. Since gas chromatography showed that this oil contained numerous components, none of which was present in large quantity, it was not investigated further. In a third reaction at  $-70^{\circ}$  using slightly less than the theoretical amount of sodium in the presence of alcohol, 71% of the starting material was recovered together with an oil (0.30g.) of similar qualitative composition to that obtained previously.

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P A R T   II.

## A. INTRODUCTION

Large organic molecules generally undergo thermal breakdown because some facile mode of decomposition is possible, as for example "unzipping" or  $\beta$ -elimination. Where no such ready pathway exists, the thermal or oxidative stability of the weakest bond in the molecule determines the upper operating temperature of the material. Previous work has shown that this point of weakness is often the C-H bond, whether this be aliphatic or aromatic, and that its replacement by a C-F bond may lead to some improvement in stability. The knowledge in this field is being extended by the preparation of aromatic polymeric materials in which all C-H bonds are replaced by C-F bonds. Very few per-fluorinated aromatic polymers have been prepared.

The aim of this part of the programme is to determine if fully fluorinated aromatic polymers offer any improvement in thermal or oxidative stability over their hydrogenic analogues. Essential preliminary work requires the preparation of fully fluorinated aromatic model compounds and their hydrogenic analogues, for comparison of the thermal decomposition temperatures in the two series of compounds. Where equal or improved stability is shown by the per-fluorinated compounds, then these structures will be incorporated into polymers and comparisons of thermal and oxidative stability will be made with the analogous hydrogenic polymers.

## B. SUMMARY

A considerable number of perfluorinated aromatic compounds and their hydrogenic analogues have been synthesised. Comparison of the thermal decomposition temperatures in the two series of compounds suggests that perfluorinated structures occasionally are more thermally stable than their hydrogenic analogues, and that certain groups (NH in a perfluorinated compound and possibly tetrafluoro-m-phenylene) lead to thermal instability. Many of the perfluorinated compounds had lower thermal decomposition temperatures than their hydrogenic analogues, but where these were equal to or higher than those of the hydrogenic analogues, polymers were prepared. The polymers were polyimides, polyhydrazides, polycarbonates and polyesters. A polyamide was prepared to check the finding of low thermal stability in secondary amide model compounds. As the polymers mostly appeared to have low molecular weights few comparisons of stability have been made. Of the polymers that were examined by heating in air, the per-fluorinated polymers were less stable than their hydrogenic analogues.

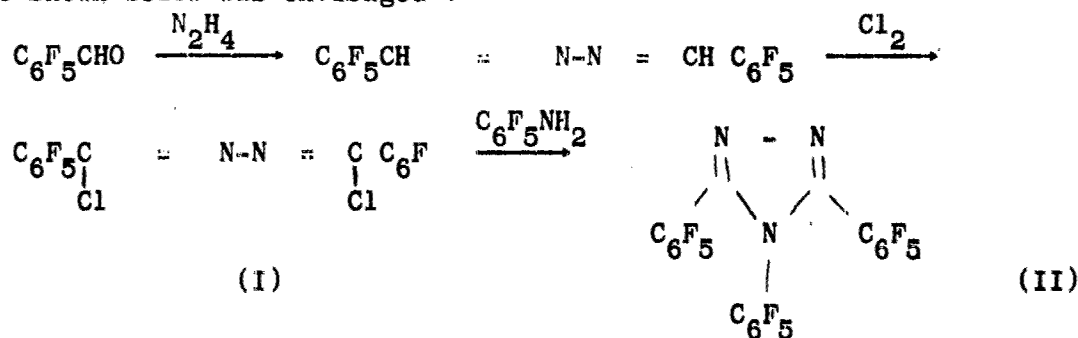
## C. DISCUSSION

### 1. SYNTHESSES OF MODEL COMPOUNDS

#### Heterocyclic Compounds

3,4,5-Triphenyl-1,2,4-triazole was obtained from N,N'-dibenzoylhydrazine and phenylphosphazanolide (from aniline and phosphorus trichloride) in boiling o-dichlorobenzene (ref. 2), but the method failed when applied to the preparation of the fluoro-analogue; unreacted N,N'-di(pentafluorobenzoyl)hydrazine (ref. 1) and 2,5-di(pentafluorophenyl)-1,3,4-oxadiazole were isolated from the reaction.

An alternative route to 3,4,5-tri(pentafluorophenyl)-1,2,4-triazole (II) consists of the reaction between di( $\alpha$ -chloropentafluorobenzylidene)hydrazine (I) and pentafluoroaniline (cf. ref. 3) and attempts have, therefore, been made to synthesise the intermediate substituted hydrazine. However, N,N'-di(pentafluorobenzoyl)hydrazine was converted into 2,5-di(pentafluorophenyl)-1,3,4-oxadiazole and not into the required intermediate, by reaction with either phosphorus pentachloride (cf. ref. 4) or with thionyl chloride and a trace of N,N-dimethylformamide, and alternative routes were investigated. Thus the route shown below was envisaged :



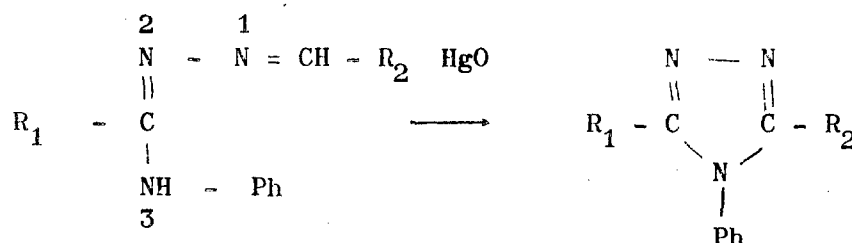
It has been confirmed that the hydrogenic analogue of the above triazole may be obtained from aniline bis( $\alpha$ -chlorobenzylidene)hydrazine. However, in dull light no chlorination of decafluorobenzalazine occurred, but chlorination under irradiation from a tungsten filament lamp yielded a compound, m.p. 85-7°, the analysis of which corresponds to the monochloro-azine. Other attempts to halogenate the azine with sulphuryl chloride, sulphuryl chloride/benzoyl peroxide, or N-bromosuccinimide failed.

Several other routes were investigated in attempts to obtain the triazole (II). One of these routes was the reaction between hexafluorobenzene



and the sodium salt of 3,5-di(pentafluorophenyl)-1,2,4-triazole in boiling pyridine. The product, m.p.  $> 340^\circ$ , was insoluble in the common organic solvents and was probably polymeric.

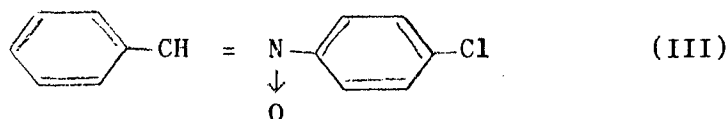
It has been reported (ref. 5) that 3,4,5-trisubstituted 1,2,4-triazoles are produced by oxidative cyclisation of  $N^1$ -arylidene derivatives of  $N^3$ -phenyl-substituted amidrazones:



$N^3$ -phenyl-substituted amidrazones have been prepared from hydrazine and  $N$ -phenyl thioamides (ref. 6), but an easier route to  $N^3$ -(pentafluorophenyl)pentafluorobenzamidrazone would be from pentafluorobenz(pentafluoroanilide) by reaction with hydrazine. To investigate this possibility a reaction between benzanilide and anhydrous hydrazine was investigated, but no reaction occurred at reflux. An attempt was also made to cyclise  $N,N$ -dibenzoylaniline to 3,4,5-triphenyl-1,2,4-triazole by reaction with hydrazine in boiling  $n$ -propanol containing a small amount of sulphuric acid, but benzanilide, m.p. and mixed m.p.  $163$ - $163.5^\circ$ , was the only product isolated. It would appear, therefore, that thioamides will be required as intermediates in this route.

A speculative reaction employing aniline,  $N,N'$ -di(pentafluorobenzoyl)-hydrazine, and phosphorus pentoxide at  $220^\circ$  gave 2,5-di(pentafluorophenyl)-1,3,4-oxadiazole (previously prepared: ref. 1).

A speculative reaction for 3,4,5-tri(phenyl)-1,2,4-triazole employed benzalazine and nitrosobenzene in ethanolic hydrogen chloride, but this gave a compound, m.p.  $181$ - $181.5^\circ$ , which is believed to be the nitrone (III), from the elemental analysis (the melting point is slightly higher than that reported in the literature; m.p.  $177.5$ - $178^\circ$  (ref. 7)).



The reported synthesis of (III) is from benzaldehyde and *p*-chloro-phenylhydroxylamine. The latter compound is obtained from nitrosobenzene and hydrogen chloride (ref. 8). Hence, it is probable that this hydroxylamine was present in the reaction mixture and that it reacted with the diethyl acetal of benzaldehyde, which could conceivably be formed from benzalazine in the presence of ethanolic hydrogen chloride.

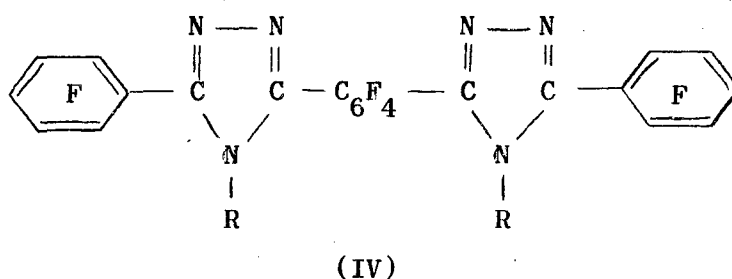
The reaction of *N,N'*-di(pentafluorobenzoyl)hydrazine with the anilinium salt of toluene-*p*-sulphonic acid at 205° gave a compound, m.p. 156-8° in low yield. There were bands in the I.R. spectrum that could be attributed to  $C_6H_5-N$ ,  $C=N$ , and  $C-F$ , which would be present in 3,5-di(pentafluorophenyl)-4-phenyl-1,2,4-triazole, but there was also possibly carbonyl absorption, although  $NH$  or  $CH_3$  groups were absent. This compound proved to be a slightly impure sample of 3,5-di(pentafluorophenyl)-4-phenyl-1,2,4-triazole, m.p. 158-9° obtained by the reaction between *N,N'*-di(pentafluorobenzoyl)hydrazine and *N*-phenylbenzenesulphonamide at 250°.

The last synthetic method has been applied to the preparation of (II) in 66% yield by treating *N,N'*-di(pentafluorobenzoyl)hydrazine with *N*-(pentafluorophenyl)benzenesulphonamide. *N*-(Pentafluorophenyl)benzenesulphonamide was obtained from the *N*-lithio derivative of pentafluoroaniline and benzenesulphonyl chloride. This route was employed because pentafluoroaniline and benzenesulphonyl chloride did not react in the presence of aqueous sodium hydroxide or in the presence of benzene/*N,N*-diethylaniline.

An attempt to prepare 3,5-di(pentafluorophenyl)-1,2,4-triazole by a method analogous to that used in the preparation of the hydrogenic analogue (ref. 1), viz. by heating pentafluorobenzhydrazide with pentafluorobenzonitrile to 230°, was unsuccessful, the product being a complex mixture. However, the triazole was obtained by the application of a general method for the preparation of 3,5-diaryl-1,2,4-triazoles reported by Potts (ref. 21). This method consisted of heating pentafluorobenzhydrazide toluene-*p*-sulphonate (obtained from the hydrazide and the sulphonic acid in ethanol) with pentafluorobenzonitrile. Satisfactory elemental analytical figures were obtained for the triazole, but those for the intermediate sulphonic acid salt of the hydrazide were not so satisfactory as regards carbon and fluorine.

An attempt to prepare 3,3'-*p*-phenylenebis (5-phenyl-1,2,4-triazole) (IV) from *p*-dicyanobenzene and benzhydrazide toluene-*p*-sulphonate was, however, unsuccessful; the product was a complex mixture. In view of this, and because of the considerably lower thermal decomposition points of 3,5-di(pentafluorophenyl)-1,2,4-triazole and 3,4,5-tri(pentafluorophenyl)-1,2,4-triazole compared

with those of their hydrogenic analogues no syntheses of bistriazoles (IV) have been attempted.



Imino ether hydrochlorides are intermediates for both 1,3,4-oxadiazoles (refs. 1,9) and 1,2,4-triazoles (ref. 10). Several attempts were made to prepare perfluoroarylimino ether hydrochlorides from pentafluorobenzonitrile and tetrafluorophthalonitrile. Although a trace of a crystalline product was obtained from pentafluorobenzonitrile, in the presence of ethanol and hydrogen chloride in ether, the product was in far too small an amount for investigation, apart from an examination of the infra-red spectrum. The spectrum had too many unassigned bands for the product to be characterised in this way.

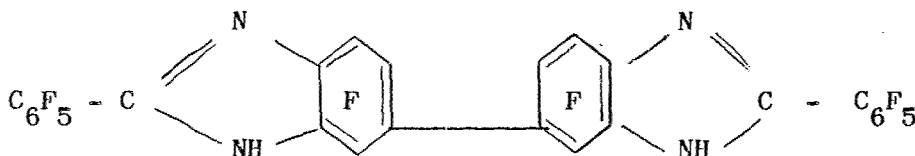
Although unsatisfactory elemental analyses were first obtained for tetrafluoroterephthalaldihydrazide there is no doubt that the compound obtained is the correct one. The compound, originally obtained from dimethyl tetrafluoroterephthalate and aqueous hydrazine (ref. 1), has now been prepared from tetrafluoroterephthaloyl chloride and anhydrous hydrazine. When the compound was treated with pentafluorobenzoyl chloride the same tetrafluoroterephthaloyl bis(pentafluorobenzhydrazide) was obtained as when tetrafluoroterephthaloyl chloride was treated with pentafluorobenzhydrazide, as shown by identical infra-red spectra. No analysis was obtained for this very high melting bisbenzhydrazide but its cyclisation product with phosphoryl chloride has analytical figures closely corresponding to those for p-di(2-pentafluorophenyl-1,3,4-oxadiazolyl-5)-benzene, a required model compound. The infra-red of this final product is not inconsistent with the bis(oxadiazole) structure.

Similarly, m-di(2-pentafluorophenyl-1,3,4-oxadiazolyl-5(tetrafluorobenzene was obtained by cyclisation of tetrafluoroisophthaloyl bis(pentafluorobenzhydrazide) with phosphoryl chloride. This bisbenzhydrazide was obtained from tetrafluoroisophthaloyl chloride and pentafluorobenzhydrazide,

but it could not be obtained via tetrafluorophthaloyl hydrazide owing to inability to synthesise the latter from hydrazine and the acid chloride. These last reactants gave what is probably a polymeric product.

In an attempt to prepare m-di(2-pentafluorophenyl-1,3,4-thiadiazolyl-5)-tetrafluorobenzene, the above bis(oxadiazole) was heated with phosphorus pentasulphide in sym.-tetrachloroethane but the bis(oxadiazole) was isolated unchanged. A similar result was obtained with p-di(2-pentafluorophenyl-1,3,4-oxadiazolyl-5)-tetrafluorobenzene. Tetrafluoroterephthaloyl bis(pentafluorobenzhydrazide) heated with phosphorus pentasulphide in sym.-tetrachloroethane gave a product that could not be recrystallised to constant melting point even though no carbonyl or NH absorption was observed in the infra-red, i.e. cyclisation would seem to have occurred, but the compound could not be obtained in the pure state.

Hexafluoro-3,3',4,4'-tetraminobiphenyl with phenyl pentafluorobenzoate did not give the required 2,2'-di(pentafluorophenyl)-5,5'-di(trifluorobenzimidazole) (V). The ester was recovered whilst the amine yielded a black solid, m.p. >320°, insoluble in common organic solvents, acid, or alkali.



(V)

Another attempt to prepare (V) by the reaction between 3,3',4,4'-tetraminohexafluorobiphenyl and pentafluorobenzoic acid in polyphosphoric acid at 175° (cf. ref. 11), gave a product of indefinite melting point and soluble in dilute aqueous alkali. Purification by recrystallisation was unsuccessful. The infra-red spectrum of the product has bands indicative of the amide group. Hence, it seems improbable that cyclisation to the benzimidazole (V) has occurred.

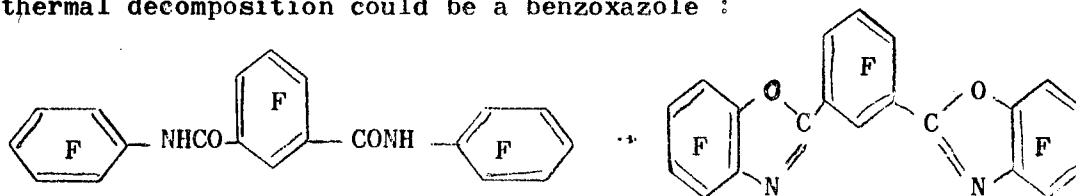
An attempt to prepare 2,2'-di(pentafluorophenyl)-5,5'-di(trifluorobenzimidazole) by reaction of 3,3',4,4'-tetraminohexafluorobiphenyl with two molar equivalents of pentafluorobenzoyl chloride and cyclisation of the mixed di(pentafluorobenzoyl) derivatives at 300° was unsuccessful. No pure compound could be isolated from the reaction products.

## Amides

Tetrafluoro-m-phenylene diamine, believed to be of 97% purity (ref. 1) was treated with pentafluorobenzoyl chloride and N,N-diethyl-aniline in benzene. A side product of higher melting point was obtained, representing 10% of the yield, in addition to the required m-di(pentafluorobenzamido)tetrafluorobenzene. The side product had a correct elemental analysis for an isomer of the main product and has bands in its I.R. spectrum attributable to a strongly hydrogen bonded secondary amide group. This compound was subsequently obtained by the reaction of tetrafluoro-p phenylene diamine with pentafluorobenzoyl chloride.

Tetrafluoroisophthaloyl chloride and pentafluoroaniline with N,N-diethylaniline in benzene gave the required tetrafluoroisophthaloyl di-(pentafluoroanilide) (VI).

However, the above perfluorinated amides are secondary amides and their low thermal decomposition points, compared with those of their hydrogenic analogues, may possibly be due to the amidic hydrogen. It is possible that hydrogen fluoride may easily be lost from such compounds. A product of such a thermal decomposition could be a benzoxazole :

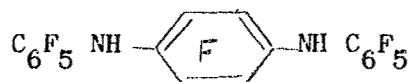


(VI)

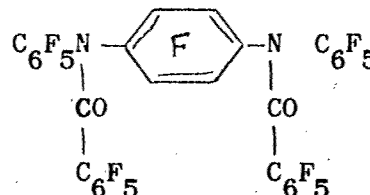
Such a reaction has not yet been checked, but if it does occur it may lead to a useful synthetic route for perfluorinated benzoxazoles. It was, therefore, of interest to investigate the thermal stability of perfluorinated tertiary amides : amides in which the amidic hydrogen had been replaced by a group of high thermal stability, e.g. a pentafluorophenyl group.

The three hydrogenic analogues of such model compounds, N,N,N',N'-tetraphenylphthalamide, N,N,N',N'-tetraphenylterephthalamide, and N,N'-dibenzoyl-N,N'-diphenyl-p-phenylene diamine, were prepared from the appropriate amine and carboxylic acid chloride in benzene containing N,N-diethylaniline. However, when these reaction conditions were employed with decafluorodiphenylamine and tetrafluoroterephthaloyl chloride no reaction occurred. The reaction of decafluorodiphenylamine with terephthaloyl chloride in pyridine gave no pure product. By converting decafluorodiphenylamine to the N-lithio derivative and treating this compound with tetrafluoroterephthaloyl chloride, the required perfluorinated bis(tertiary amide) was obtained. Because the simple methods

of preparation could not be employed with decafluorodiphenylamine it may be that polyamides of similar structure will be difficult to obtain. However, if the appropriate diamine,  $N,N'$ -di(pentafluorophenyl)tetrafluoro-*p*-phenylene diamine (VII) becomes available, this will be checked, but the corresponding tertiary amide (VIII) will first be synthesised from the diamine, as a model compound.



(VII)



(VIII)

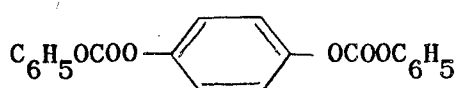
### Imides

Tetrafluoro-*m*-phenylene diamine with tetrafluorophthaloyl chloride in benzene containing diethylaniline yielded a main product, *m*-di(tetrafluorophthalimido)tetrafluorobenzene (A), along with small amounts of two side products (B) and (C). The side product (B) did not melt below 400° and as it was insoluble in most solvents it was thought to be a polyamide. However, the absence of NH absorption in the infra-red spectrum showed that (B) was not a polyamide, and the compound was subsequently synthesised by treating tetrafluoro-*p*-phenylene diamine with tetrafluoro phthalic anhydride or with tetrafluorophthaloyl chloride. Hence, (B) is *p*-di(tetrafluorophthalimide)tetrafluorobenzene, and the melting point was found to be above 516°. The compound (C) has elemental analysis figures closely corresponding to the calculated values for (A), and (C) also has an infra-red spectrum similar to that of (A). Hence (C) appears to be an isomer of (A) and (B). Gas chromatographic examination of the tetrafluoro-*m*-phenylene diamine had originally indicated the compound to be 97% pure (ref. 1), but since the results of the above syntheses were obtained further gas chromatographic examination was carried out. This showed that the tetrafluoro-*m*-phenylene diamine contained the para isomer (ca. 15%) and the ortho isomer (ca. 5%) along with pentafluoroaniline (ca. 1%). These percentages are approximate only, being derived from measurements of peak areas in the chromatograms. The evidence therefore, points to (C) being the ortho isomer of (A) and (B), but this has not been proved.

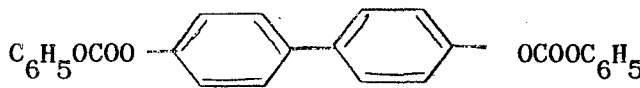
## Carbonates

Pentafluorophenyl chloroformate was prepared from pentafluorophenol and phosgene in the presence of N,N-diethylaniline in ether. By heating the chloroformate with octafluoro-4,4'-dihydroxybiphenyl a crystalline compound was obtained. This is believed to be di(pentafluorophenyl)octafluoro-4,4'-biphenylene biscarbonate, i.e. the perfluorinated analogue of (X). When an attempt was made to determine its thermal decomposition point this compound showed irregular variations of vapour pressure with temperature. This behaviour has been noted previously when a compound is impure. In this case, the compound had been recrystallised to constant melting point.

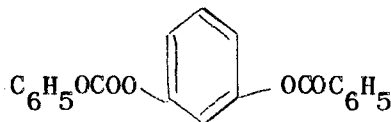
Pentafluorophenyl chloroformate with tetrafluorohydroquinone or tetrafluororesorcinol also gave crystalline compounds, believed to be the perfluorinated analogues of (IX) and (XI). However, although di(pentafluorophenyl) tetrafluoro-m-phenylene biscarbonate could be recrystallised to constant melting point, this was not true of the p-isomer and no elemental analysis was obtained. Poor fluorine analyses were obtained for the other perfluorinated biscarbonates, although the analyses for carbon were satisfactory.



(IX)



(X)



(XI)

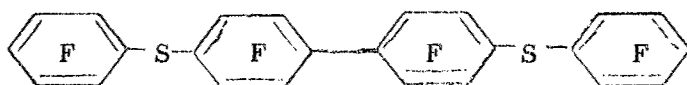
The hydrogenic carbonates (IX) and (X) have been prepared earlier (ref. 1). The action of heat on these compounds has been further investigated. It was reported (ref. 1) that these compounds re-solidify just above the m.p. (160-170°) to what is probably a polymer, and this solid does not remelt up to 400°. Samples of (IX) and (X) have now been heated in Pyrex tubes for 1½ hr. at 250° without solidification but samples in soda glass tubes inserted in a bath at 250° first melted and then re-solidified in a few minutes, with effervescence. The substances, freed from low molecular weight compounds by extraction with ether and petrol, had infra-red spectra similar to the spectra

of (IX) and (X). Hence the solids appeared to be polycarbonates. A German Patent (ref. 12) describes the pyrolysis of such biscarbonates to give polycarbonates with loss of diphenyl carbonate. The above results indicate that the polymerisation is probably base catalysed. The ethereal extract from the pyrolysis of (IX) gave a compound, m.p. 77-9°, shown to be diphenyl carbonate from the infra-red spectrum.

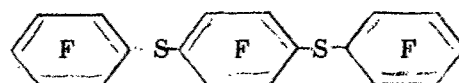
Because (IX) and (X) appeared to be relatively thermally stable in Pyrex glass, re-preparations of these compounds were carried out, as described previously (ref. 1), in the expectation that thermal decomposition points could be determined. In an attempt to purify (IX) by distillation polymerisation occurred, but the melting point of (X) was raised by distillation, and only a small amount of polymeric material remained in the still. However, during an attempt to determine the  $T_D$  of (X) the sample polymerised in the isoteniscope bulb (Pyrex) after 2½ hr. at elevated temperature (330-361°). Therefore, the  $T_D$  of these compounds cannot be determined in the apparatus available, and no comparison is strictly possible between (IX) and (X) and their perfluorinated analogues, because the decomposition of (IX) and (X) is apparently not purely thermal even in Pyrex glass.

#### Sulphides

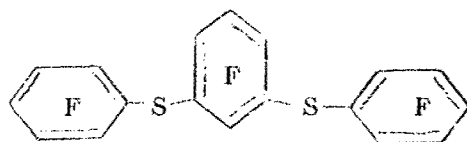
Attempts have been made to prepare the sulphide (XII)



(XII)



(XIII)



(XIV)



Pentafluorophenylsulphenyl chloride was obtained by the reaction of chlorine with di(pentafluorophenyl) disulphide (obtained as described by Tatlow et al, ref. 13) or from chlorine and pentafluorothiophenol. No reaction occurred between the sulphenyl chloride and 2,2',3,3',5,5',6,6'-octafluorobiphenyl in the presence of aluminium bromide in carbon disulphide. The sulphenyl chloride was added to 4,4'-dilithiooctafluorobiphenyl in ether/tetrahydrofuran, and the mixture was treated with dilute hydrochloric acid. Di(pentafluorophenyl)disulphide was isolated, along with an ethanol-insoluble portion of indefinite melting point. No pure compound could be obtained by recrystallisation from petrol. In a repetition of this experiment similar products were obtained and it was established that the chief product of indefinite m.p., had no absorption due to  $\text{CH}_2$  in the infra-red. Hence the chief product is not derived from the solvents and it is possibly a polymeric sulphide formed as a result of the high reactivity of first formed octafluoro-4,4'-di(pentafluorophenylthio)-biphenyl towards 4,4'-dilithiooctafluorobiphenyl.

An attempt was made to prepare di(pentafluorophenyl)sulphide, a compound analogous to (XII), (XIII) and (XIV), from a pentafluorobenzene diazonium salt and sodium pentafluorothiophenoxide (cf. ref. 14). An oil was obtained which yielded di(pentafluorophenyl)disulphide on distillation. It is not clear whether the disulphide was produced during the reaction or was present as an impurity in the pentafluorothiophenol.

Cuprous thiophenoxide reacted with m-dibromobenzene in quinoline/pyridine at 200-210° to give 1,3-di(phenylthio)benzene, the hydrogenic analogue of (XIV) in 87% yield (cf. ref. 15). The hydrogenic analogues of (XII) and (XIII) were synthesised earlier (ref. 1).

Imperial Smelting Corporation have now supplied the sulphides (XII), (XIII), and (XIV) as a result of non-contract synthetic work. Therefore, further investigations of syntheses of these compounds are not required.

#### Esters

Satisfactory elemental analyses have now been obtained for 4,4'-di(pentafluorobenzoyloxy)octafluorobiphenyl and di(pentafluorophenyl) tetrafluoroterephthalate. These compounds were synthesised earlier and had unsatisfactory analyses (ref. 1).

Tetrafluoroisophthaloyl chloride was obtained from the acid by means of thionyl chloride containing a trace of dimethylformamide. The dimethyl ester was prepared from the acid chloride and shown to be ca. 98%

pure, with 2% high boiling material, by gas chromatography. The acid chloride was assumed to have this order of purity, and was converted to the di(pentafluorophenyl)ester in benzene containing the phenol and an equivalent of N,N-diethylaniline. Gas chromatography showed the ester to be ca. 95% pure after recrystallisation, with two or three peaks of lower retention time.

Another preparation of tetrafluoroisophthalic acid was similarly converted to the acid chloride. This appeared to contain less impurity than the chloride obtained as above; the dimethyl ester was at least 99% pure by gas chromatography (i.e. no impurity was observed, but 1% was probably the lowest quantity that would be observable under the conditions used). However, the di(pentafluorophenyl)ester was prepared and although recrystallised to a higher melting point than that above it was shown to contain ca. 1.5% impurity by gas chromatography.

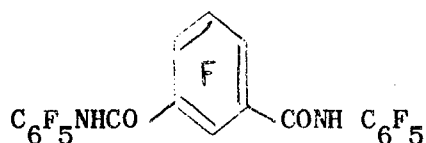
Tetrafluororesorcinol with pentafluorobenzoyl chloride in benzene containing N,N-diethylaniline gave 1,3-di(pentafluorobenzoyloxy)tetrafluorobenzene. The fluorine analysis was low, but the carbon figure was within acceptable limits.

## 2. Thermal Decomposition Points of Model Compounds

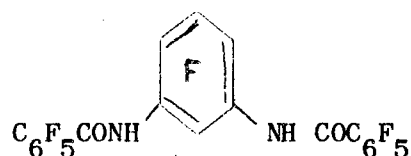
The thermal decomposition points ( $T_p$ ) are as defined by Blake et al and have been measured in apparatus similar to that used by those workers (ref. 16). So obtained, the  $T_p$  is the temperature at which the vapour pressure of the compound increases at a rate of 0.84 mm. Hg min.<sup>-1</sup> in a nitrogen atmosphere. The method requires that the compounds be liquid at the temperature corresponding to this rate of vapour pressure increase.

Table 1 combines the results obtained earlier (ref. 1) with those now reported (apart from those of secondary amides). The table is constructed so that comparisons of  $T_p$  may be made between analogous hydrogenic and perfluorinated compounds, or between classes of compounds.

Secondary amide model compounds have not been included in Table I because the perfluorinated secondary amides were too thermally unstable at their melting points for their  $T_p$  to be determined. Two such amides, tetrafluoroisophthaloyl di(pentafluoroanilide) (XV) and m-di(pentafluorobenzamido) tetrafluorobenzene (XVI) have been investigated. For (XV) at 331° the rate of vapour pressure increase was ca. 273 mm. Hg min.<sup>-1</sup>, whereas the  $T_D$  of isophthaloyl dianilide was 328° (ref. 1). For (XVI) the rate of vapour pressure increase was 13.6 mm. Hg min.<sup>-1</sup> at 302°, whereas the  $T_D$  of m-dibenzamidobenzene was 321° (ref. 1).



(XV)



(XVI)

Other perfluorinated secondary amides and those secondary amides prepared from hydrogenic acids with perfluorinated amines, or from hydrogenic amines with perfluorinated acids have had their thermal stability results collected elsewhere (ref. 1). As noted in Section (1), the perfluorinated secondary amides may owe their thermal instability to the presence of the remaining amidic hydrogen. When the hydrogen was substituted by a pentafluorophenyl group to give a tertiary amide, in one case, the thermal stability was markedly increased : see line 21 of Table I.

Similarly, a higher  $T_D$  was obtained by substituting a pentafluorophenyl group for the imino hydrogen in the 1,2,4-triazole series : see lines 3 and 4 in Table I. Nevertheless, 3,4,5-tri(pentafluorophenyl)-1,2,4-triazole has a lower  $T_D$  than its hydrogenic analogue.

In view of these observations for perfluorinated compounds containing the NH group it seems probable that the perfluorinated analogue of 2,2'-diphenyl-5,5'-di(benzimidazole) (XVII; where  $R = NH$ ) will have a low  $T_D$ . On the other hand, the perfluorinated compounds XVII ( $R = NC_6H_5$ , O or S) may well have high  $T_D$  values.

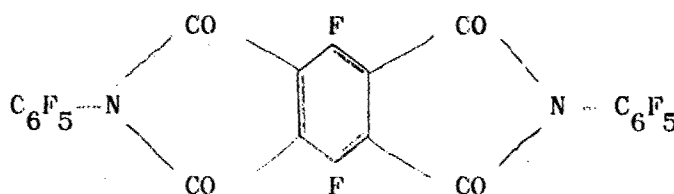


(XVII)

A comparison of the thermal decomposition points of diphenyl-*m*-phenylene biscarbonate (XI) and its perfluorinated analogue has been possible even though the  $T_D$  of the latter could only be estimated, owing to the compound having a low boiling point. It was not possible to determine the  $T_D$  for two other hydrogenic carbonates (IX) and (X) because of their ready polymerisation. This is referred to in Section A. Hence, it is not possible to compare the  $T_D$  figures of (IX) and (X) with those of their perfluorinated analogues, and as these perfluorinated carbonates are difficult to obtain in the pure state it is proposed that further comparisons of carbonate structures be made on polycarbonates.

From Table I (line 13) it will be noted that the perfluorinated carbonate has a higher  $T_D$  than its hydrogenic analogue. This carbonate contains the tetrafluoro-*m*-phenylene group and is the one instance from the table where a compound containing this group has a higher  $T_D$  than its hydrogenic analogue. In other cases (lines 5, 8, 10, 15, 18) where the tetrafluoro-*m*-phenylene group occurs the  $T_D$  is lower than that of the corresponding compound with a *m*-phenylene group. Further comparisons show that the tetrafluoro-*m*-phenylene group depresses the  $T_D$  more than do the tetrafluoro-*o*-phenylene, tetrafluoro-*p*-phenylene, or octafluoro-4,4'-bisphenylene groups (see lines 5 and 6; 7, 8 and 9; 10, 11 and 12; 15, 16 and 17). It would be desirable to have further examples of model compounds to decide if this is a common feature in the perfluorinated aromatic series. Table II shows an example of a tetrafluoro-*m*-phenylene group in a polyester, where the stability in air at 300° is lower than that of the corresponding polyester with the tetrafluoro-*p*-phenylene group.

As for the imides the evidence for thermal stability, as far as it exists, is conflicting. When difluoropyromellitic anhydride is available it will be converted to the di-imide (XVIII), although it does appear that the presence of the two hydrogen atoms in the analogous *N,N'*-di/pentafluorophenyl)pyromellitimide is not detrimental to thermal stability (see  $T_D$  value : Table I, line 19). The other imide model compound contains the tetrafluoro-*m*-phenylene group (Table I, line 18).



(XVIII)

Table I shows that the perfluorinated esters have lower thermal decomposition points than their hydrogenic analogues. In some cases the difference between the  $T_D$  figures is small, and it will be appropriate to prepare polyesters for further comparisons.

TABLE I

Pair No.	Skeletal Structure	Hydrogenic Compound $T_D$	Perfluorinated Compound $T_D$
1		304°C	327°C
2		301°C	343°C
3		279°C	212°C
4		352°C	305°C
5		300°C	285°C
6		302°C (note a)	304°C
7		307°C	297°C
8		362°C	300°C (note b)

TABLE I (Contd.)

Pair No.	Skeletal Structure	Hydrogenic Compound $T_D$	Perfluorinated Compound $T_D$
9		353 °C	318-324 °C
10		335 °C	304 °C
11		332 °C	299 °C
12		327 °C	320 °C
13		278 °C	ca. 330 °C (note c)
14		(polymerised during the determination)	329 °C (292 °C) (note d)

TABLE I (Contd.)

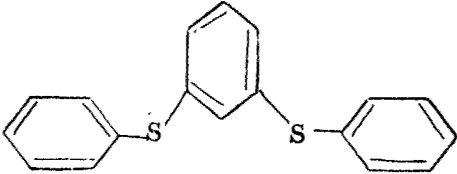

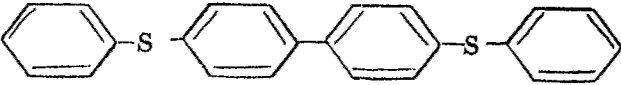
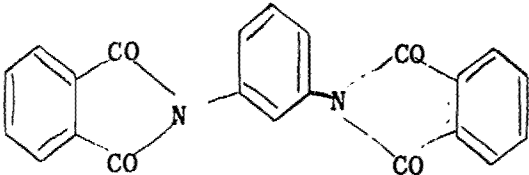
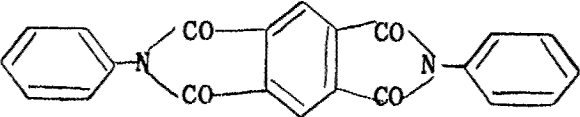
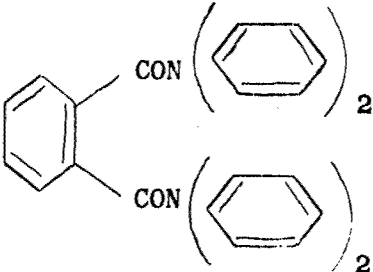
Pair No.	Skeletal Structure	Hydrogenic Compound $T_D$	Perfluorinated Compound $T_D$
15		375°C	324°C
16		365°C	328°C
17		371°C	336°C
18		390°C	318°C
19		<m.p. (note e)	418°C (note f)
20		294°C	



TABLE I (Contd.)

Pair No.	Skeletal Structure	Hydrogenic Compound $T_D$	Perfluorinated Compound $T_D$
21		318°C (note g)	340°C (note h)
22		334°C	—
23		432°C	—

### Notes to Table I

- (a) This  $T_D$  was obtained by extrapolation of the vapour pressure/temperature curve below the m.p.
- (b) 98.5% pure by gas chromatography.
- (c) This is a rough indication of the  $T_D$ . Because of the volatility if this compound an attempt was made to determine the  $T_D$  under pressure, but the temperature could not be raised higher than 326°C with the pressure of mercury available. At 326°C the rate of increase in vapour pressure was 0.5 mm. Hg min<sup>-1</sup>.
- (d) The divergent values perhaps indicate impurities in the sample, leading to irregularities in the vapour pressure/temperature relationship.
- (e)  $T_D$  is lower than m.p. 454°C but is probably of the same order as that of the fluoro analogue judged by comparison of the rates of vapour pressure increase at 456°C.
- (f) This is not a perfluoro compound. It is N,N'-di(pentafluorophenyl)-pyromellitimide.
- (g) The hydrogenic secondary amide  $p\text{-C}_6\text{H}_4(\text{CONHC}_6\text{H}_5)_2$  corresponding to this tertiary amide had a rate of vapour pressure increase of 4.9 mm. Hg/min. at 354°C (ref. 1).
- (h) The perfluorinated secondary amide  $p\text{-C}_6\text{F}_4(\text{CONHC}_6\text{F}_5)_2$  corresponding to this tertiary amide had a rate of vapour pressure increase of 100 mm. Hg/min. at 324°C. (ref. 1).

### 3. The Preparation of Polymers

#### Polyesters

Poly(4,4'-biphenylene isophthalate), poly(4,4'-biphenylene terephthalate), and their perfluorinated analogues have been prepared by the interfacial condensation method from the dihydric phenol in aqueous alkaline solution and the acid chloride in trichloroethylene (cf. ref.17).

The hydrogenic polymers were found to contain inorganic residues on analysis. On the other hand, the perfluorinated analogues had no inorganic residues. Only one of these polymers gave satisfactory analytical figures, and this was from a repeat analysis.

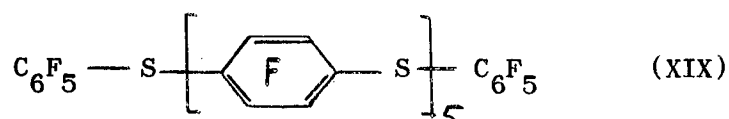
All of the polyesters had low inherent viscosities (see Table II); those of the perfluorinated polyesters were particularly low, suggesting low molecular weights. However, little or no hydroxyl absorption (by end groups) was observed in the infra-red spectra.

### Polyamides

Poly(m-phenylene terephthalamide) and its perfluorinated analogue were prepared by the interfacial method, with the diamine in aqueous alkaline solution and the acid chloride in carbon tetrachloride. They had unsatisfactory analytical figures for the elements, and the inherent viscosity of the perfluorinated polyamide was low (0.04) as compared with that (0.41) for the hydrogenic polyamide, in 98% sulphuric acid. This suggests that the perfluorinated polymer had a low molecular weight.

### Polysulphides

Poly(tetrafluorophenylene sulphide) was prepared from sodium pentafluorothiophenate and hexafluorobenzene in pyridine (as described : ref. 13). The elemental analysis suggests the structure (XIX) for this polymer.



### Polycarbonates

Polycarbonates have been prepared from resorcinol, hydroquinone, and 4,4'-dihydroxybiphenyl by the reaction of each with phosgene. The interfacial condensation method (ref. 24) was employed in sym. tetrachloroethane/aqueous sodium hydroxide. The polycarbonate from resorcinol had a low inherent viscosity (0.12), but the inherent viscosities of the other two polycarbonates could not be determined owing to their insolubility. The same interfacial technique was applied to the preparation of the perfluorinated polycarbonates. This was successful with octafluoro-4,4'-dihydroxybiphenyl, but not with tetrafluororesorcinol or tetrafluorohydroquinone. The latter

compound appeared to be too reactive towards the aqueous sodium hydroxide so that a dark reaction mixture was obtained and no polymer was isolated. Only a low yield of polymer was obtained from tetrafluororesorcinol, again the reaction mixture became dark, and the polymer had a very low inherent viscosity (0.03). No darkening occurred during the preparation of the polycarbonate derived from octafluoro-4,4'-dihydroxyoctafluorobiphenyl, but the inherent viscosity was again very low (0.02) and there was a 40% weight loss on heating it to 330° in a platinum crucible in air.

All of the polycarbonates prepared as described above had unsatisfactory analyses. The polycarbonates from resorcinol and hydroquinone contained inorganic residues, whilst that from 4,4'-dihydroxybiphenyl contained chlorine (1%).

An alternative route to polycarbonates would be the reaction of a bischloroformate of the dihydric phenol with the dihydric phenol, in the absence of strong alkali. A bischloroformate has already been prepared (ref.1) from tetrafluorohydroquinone, but in low yield and doubtful purity. It was thought that a bischloroformate could be obtained from octafluoro-4,4'-dihydroxybiphenyl in higher yield and better purity as the product should be more easily crystallised. However, the reaction of this dihydric phenol with phosgene in ether containing N,N-diethylaniline gave a product that could not be purified by recrystallisation, and on attempted distillation decomposition occurred to yield a high melting solid. Presumably phosgene had been eliminated to yield a polycarbonate. This dissolved in moist amidic solvents e.g. hexamethylphosphoramide with slight effervescence, but was insoluble in dimethyl sulphoxide. A sample of the substance in a platinum crucible was heated in air at 220° until the rate of weight loss was very low. Further heating in air at 330° caused a rapid loss in weight.

### Polyimides

Polyamic acids were obtained by treating di-amines in dimethylacetamide solution with pyromellitic dianhydride. Conversion to polyimides was achieved by evaporation of the solvent and heating the film produced at 300°, first in air at atmospheric pressure, and then in vacuo. The di-amines employed were m- and p-phenylene diamine, benzidine, and the three perfluorinated analogues of these di-amines. Only in the case of the polyimide derived from tetrafluoro-m-phenylene diamine was a satisfactory elemental analysis obtained. The polyamic acid derived from benzidine had a reasonably high inherent viscosity (0.47 at 1% concentration in dimethylacetamide) compared with a low inherent viscosity for the polyamic acid derived from octafluorobenzidine (0.06 at 0.5% concentration in dimethylacetamide).

It is clear that optimum reaction conditions will have to be determined to obtain polyimides of higher molecular weight. By the carefully controlled addition of pyromellitic dianhydride to m-phenylene diamine an inherent viscosity of 0.85 was attained, in N-methylpyrrolidone that had been dried over molecular sieve.

### Polyhydrazides

Polyhydrazides have been obtained from di-acid chlorides by reaction with hydrazine in dimethylacetamide solution. The chlorides employed were those of terephthalic, isophthalic, tetrafluoroterephthalic and tetrafluoroisophthalic acids. The bishydrazide of the last named acid also yielded the polyhydrazide by reaction with tetrafluoroisophthaloyl chloride in dimethylacetamide. As described in the literature (ref.18) the polyhydrazide from terephthaloyl chloride was insoluble. Otherwise all the other polyhydrazides were soluble in such solvents as dimethylacetamide and dimethyl sulphoxide, and their inherent viscosities were relatively low (ca. 0.1 to 0.2). As the thermal stability of these polymers may be a function of molecular weight (particularly in the case of perfluorinated polymers where end-groups may react with nuclear fluorine), it was considered advisable to attempt to prepare polyhydrazides with higher inherent viscosities. Accordingly, preparations of polyhydrazides from tetrafluoroterephthaloyl chloride and isophthaloyl chloride were carried out in N-methylpyrrolidone, or in N-methylpyrrolidone containing lithium chloride, but the polymers had only slightly higher inherent viscosities. The polyhydrazides appeared to retain moisture even when dried at 100°/0.1 mm. This is suggested by the elemental analyses, and in the case of poly(isophthalhydrazide) by its weight loss curve on the thermobalance. The curve shows a loss in weight in air up to ca. 290° that is suggestive of dehydration, followed by a further loss in weight indicative of cyclisation to the poly(oxadiazole).

When a larger quantity of poly(isophthalhydrazide) was heated at 280° for 30 min. in vacuo an insoluble product was formed, the infra-red spectrum of which was consistent with poly(oxadiazole). A sublimate was also formed, which from the infra-red spectrum appeared to be impure isophthalic acid. This may have arisen by the hydrolysis of isophthaloyl chloride by moisture in the solvent used for the preparation of the polymer.

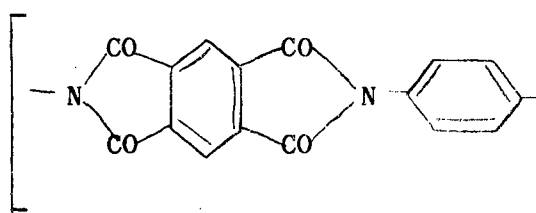
The dimethylacetamide and N-methylpyrrolidone used for the preparation of polyhydrazides contained 1 to 2% of water (infra-red determination) even though these solvents had been dried over calcium oxide and fractionated. It is possible that moisture in the solvents may have been the cause of the formation of polymers of low molecular weight. Further preparations of polyhydrazides will be carried out when dry solvents are available.

#### 4. Polymers Heated in Air

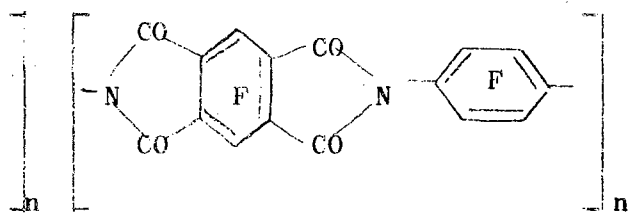
The thermal and oxidative stability of a polymer may well be a function of its molecular weight. Before comparisons of thermal and oxidative stability are made it would be desirable to know the molecular weight ranges of the polymers described in this report. In the mean time inherent viscosity has been taken as indicating relative molecular weights, and on this basis the perfluorinated polymers have lower molecular weights than their hydrogenic analogues. For this reason few experiments have so far been made on the thermal and oxidative stability of polymers.

However, six polymers were so investigated, with the results shown in Table II (Section D, 14). At 300°C in air the perfluorinated polymers lost much more weight in a given time than did the hydrogenic polymers. It should be noted that the inherent viscosities of the perfluorinated polymers are particularly low, so that these results alone should not be taken as indicating that these perfluorinated structures are considerably less stable than their hydrogenic analogues. This preliminary result requires verification. There are, however, parallels with  $T_D$  results for model structures. In the polyester with greatest weight loss the tetrafluoro-m-phenylene group occurs, and the high weight loss from the perfluorinated polyamide could be expected (see Section C 2). This polyamide was prepared and tested to check the findings with model compounds containing the secondary amide group.

Small samples of two polyimides (XXX) and (XXXI) placed in an alumina crucible were heated in air, in the furnace of a thermogravimetric balance. The weight loss of the perfluorinated polyimide at 402°C was greater than that of the hydrogenic polyimide at 450°C. The results are reported in Section D, 14. However, it should be noted that the molecular weight range of these polyimides is unknown, and it is possible that the perfluorinated polymer had a much lower molecular weight than had the hydrogenic polymer. The preparations of these polymers are to be repeated and an attempt will be made to determine their ranges of molecular weight.



(XXX)



(XXXI)

D. EXPERIMENTAL

1. ACID CHLORIDES

Tetrafluorophthaloyl chloride (cf. ref. 1 for previous preparation)

(a) Tetrafluorophthalic acid (29.5 g.), thionyl chloride (57 ml.) and N,N-dimethylformamide (0.5 ml.) were boiled under reflux during 16 hours. Excess of thionyl chloride was distilled off, and the residue because of its boiling range of 98-110°/12 mm. was re-treated with thionyl chloride (20 ml.) and N,N-dimethyl formamide (0.5 ml.) under reflux during 24 hours. The thionyl chloride was distilled off and the acid chloride was distilled.

<u>Fraction</u>	<u>b.p.</u>	<u>wt.</u>
1	94-102°/12 mm.	1.3 g.
2	103-5°/12 mm.	2.7 g.
3	106-8°/12 mm.	16.7 g.
Residue		9.7 g.

Fraction (3) was used for the tetrafluorophthalimidation of tetrafluoro-m-phenylene diamine, and for the preparation of di(pentafluorophenyl) tetrafluorophthalate. A sample of this fraction was converted to the dimethyl ester. No impurity was detected in the dimethyl ester, hence the acid chloride fraction (3) was regarded as being pure. Gas chromatographic conditions : a 10 foot column of poly(ethylene adipate) on Embacel at 200° with a helium flow rate of 100 ml./min., employing a katharometer detector.

(b) In a similar preparation to that described under (a), the acid (20 g.) yielded the acid chloride (8.5 g.), b.p. 116-118°/17 mm. (second distillation).

A sample of the acid chloride was converted to the dimethyl ester, which was found to contain an impurity of longer retention time than the main peak. The acid chloride was at least 95% pure on this basis, and was used for the tetrafluorophthalimidation of tetrafluoro-p-phenylene diamine.



### Tetrafluoroisophthaloyl chloride

(a) A solution of tetrafluoroisophthalic acid (24 g.) in thionyl chloride (50 ml.) and N,N-dimethylformamide (0.3 ml.) was boiled under reflux for 22 hr. The excess of thionyl chloride was removed by distillation and the product was distilled under reduced pressure. After several hours at room temperature the product deposited a small amount of solid (probably unreacted acid) and it was, therefore, redissolved in thionyl chloride (25 ml.) and N,N-dimethylformamide (0.3 ml.) and heated on the steam bath for 17 hr. The excess of thionyl chloride was removed by distillation and distillation of the residue gave the acid chloride (15.5 g.), b.p. 95-97°/7 mm.

Anal. Calc. for  $C_8Cl_2F_4O_2$  : C, 34.95; H, 0.0; Cl, 25.8; F, 27.65%

Found : C, 36.55; H, 0.0; Cl, 25.3; F, 26.65%

The tetrafluoroisophthaloyl chloride (0.6 g.) was boiled under reflux with anhydrous methanol (2.5 ml.) during 15 mins. The solution was added to water to yield an oil which rapidly solidified (0.6 g.), m.p. 37.8-39°. Examination by gas chromatography (4 foot column of 8.8% poly (ethylene adipate) /Embacel programmed at 10°/min. over 100-240°, with an argon flow rate of 80 ml./min. and a kathetometer detector) and was found to contain ca. 2% of a slightly higher boiling material.

(b) The acid (27 g.) from a different preparation to that used under (a), thionyl chloride (75 ml.), and dimethylformamide (0.5 ml.) were boiled under reflux overnight. The excess of thionyl chloride was distilled off and the product was distilled under reduced pressure. The distillate had a wide boiling range (60-115°/20 mm.) so that it was re-treated with thionyl chloride/dimethylformamide, and distilled :

Fraction 1, b.p. 90-105°/20 mm.

" 2, b.p. 105-110°/20 mm.

" 3, b.p. 112-114°/18 mm. (24.5 g.)

The tetrafluoroisophthaloyl chloride was converted to the dimethyl ester in anhydrous methanol and the solution was analysed by gas chromatography as in (a). The ester appeared to be at least 99% pure so that the acid chloride could be assumed to have this purity.

### Tetrafluoroterephthaloyl Chloride

This compound has been prepared previously (ref. 1). By the same method tetrafluoroterephthalic acid (38 g.), re-distilled thionyl chloride (65 ml.), and dimethylformamide (0.5 ml.) yielded the acid chloride (39.8 g.), b.p. 104°/15 mm., m.p. 34-6°; a fore-run, b.p. 98-103°/15 mm. was discarded.

A sample of the acid chloride was converted to the dimethyl ester and examined by gas chromatography. One impurity (<1%) of shorter retention time than the main peak was observed. Conditions : a 4 foot column of 8.8% poly(ethylene adipate) on Emabacel, a flow of argon of 100 ml./min., programmed from 60° to 220°C rising at 10°/min., employing a katharometer detector.

## 2. HETEROCYCLICS (AND INTERMEDIATES)

### Pentafluorobenzhydrazide (ref. 22)

Pentafluorobenzoyl chloride (7.5 g.) in anhydrous ether (75 ml.) was added dropwise to a well stirred mixture of 95% hydrazine (2.2 g.) and anhydrous ether during 25 mins. at -2 to 5°. The cooling bath was removed and the mixture was allowed to stir, first rising to room temperature over 30 mins., and then during 30 min. at room temperature. The mixture was filtered and the white solid collected was dried in the vacuum desiccator (4.7 g.). The filtrates were distilled to one third volume, to yield needle shaped crystals of pentafluorobenzhydrazide (2.3 g.), m.p. 137.5-139°. Evaporation of the mother liquors to dryness yielded crystals (1.9 g.), m.p. 127-132°.

The above solid (4.7 g.) was extracted with benzene to yield pentafluorobenzhydrazide (0.25 g.), m.p. 132.4°, and the residue was treated with hot water to dissolve hydrazine hydrochloride. The remaining solid was collected by filtration, washed with water and dried. The infra-red spectrum, m.p., and mixed m.p. 268.5-269.5° indicate this product to be N,N-di(pentafluorobenzoyl)hydrazine (ref. 1).

Recrystallisation of the impure fractions (1.9 g. + 0.25 g.) from benzene yielded pentafluorobenzhydrazide (1.95 g.), m.p. 131.5-135°.

### 3,4,5-Triphenyl-1,2,4-triazole

(a) Phosphorus trichloride (1.92 ml.) was added to a stirred solution of aniline (11 ml.) in o-dichlorobenzene (45 ml.) and the mixture was heated for 15 min. on the steam bath.  $N,N'$ -Dibenzoylhydrazine (4.8 g.) was added and this mixture was boiled under reflux with stirring for 3 hours. The product was stirred with 2N hydrochloric acid for 30 min. on the steam bath, and the solid was collected by filtration and washed with water. Recrystallisation from aqueous acetic acid yielded colourless needles (3.74 g.), m.p. 300-301°/lit. m.p. 299-300° (ref. 2) Addition of water to the mother liquors from the recrystallisation precipitated a second crop of 3,4,5-triphenyl-1,2,4-triazole (0.9 g.), m.p. 297-299°.

(b) A solution of di-( $\alpha$ -chlorobenzylidene)hydrazine (ref. 4 and 19) (1.8 g.) and aniline (0.6 ml.) in pyridine (50 ml.) was boiled under reflux for 1 hr. The triazole (0.85 g.), m.p. 300°, separated from the cold solution.

(c) (Attempted preparation)

Dry hydrogen chloride was passed into ethanol (25 ml.) for 15 min. Benzalazine (2 g.) and nitrosobenzene (1 g.) were added and the solution was kept at room temperature for 4 days. A small quantity of insoluble material was removed by filtration and the ethanolic filtrate was added to an excess of water. The precipitated solid was collected, washed with water and recrystallised three times from light petroleum (b.p. 100-120°) to give colourless needles, m.p. 181-181.5°.

Found : C, 67.85; H, 4.47; N, 6.02; Cl, 15.04% which indicates an empirical formula of  $C_{13}H_{10}ClNO$ .

The I.R. spectrum indicates that the compound is not a salt and that OH, NH or CH groups are not present. The compound is probably the nitron (III) : see Discussion.

(d) (Attempted preparation)

$N,N$ -Dibenzoylaniline (ref. 6) (6.0 g.), anhydrous hydrazine (495%) (1.0 ml.), conc. sulphuric acid (0.3 ml.) and n-propanol (100 ml.) were boiled under reflux for 5.5 hr. When cold, benzanilide, m.p. and mixed m.p. 163-163.5°, separated from the solution.

3,5-Di(pentafluorophenyl)-4-phenyl-1,2,4-triazole

(a) A mixture of  $N,N'$ -di(pentafluorobenzoyl)hydrazine (2.1 g.) and  $N$ -phenylbenzenesulphonamide (1.2 g.) was heated at  $250^\circ$  for 2 hr. The product was washed with water (30 ml.) and extracted with hot light petroleum (b.p.  $100-120^\circ$ ). The residue produced by evaporation of the petrol extract was recrystallised from benzene, then from benzene-ethanol and finally twice from light petroleum (b.p.  $100-120^\circ$ ) to give the triazole as colourless plates, (0.25 g.) m.p.  $158-159^\circ$ . The m.p. of a mixture of this compound with that obtained from  $N,N'$ -di(pentafluorobenzoyl)hydrazine and aniline toluene- $p$ -sulphonate (see (b) below) was  $155-159^\circ$ .

Calc. for  $C_{20}H_5F_{10}N_3$  : C, 50.4; H, 1.0; F, 39.8; N, 8.8

Found : C, 51.55, 50.5; H, 0.85, 0.95; F, 39.05;  
N, 8.7%

(b) A mixture of  $N,N'$ -di(pentafluorobenzoyl)hydrazine (2.1 g.) and aniline toluene- $p$ -sulphonate (1.42 g.) was heated under reflux at  $205^\circ$  for 2.5 hr. A solution of the product in benzene was washed successively with water, dil. hydrochloric acid and again with water, and was dried ( $MgSO_4$ ). Evaporation of the benzene produced a black tar which was partially soluble in light petroleum (b.p.  $100-120^\circ$ ). Evaporation of the petrol extract gave a black gum, which on recrystallisation three times from benzene gave colourless needles (0.2 g.), m.p.  $156-158^\circ$  with previous softening. The m.p. on admixture with the product of (a) was  $155-9^\circ$ . The I.R. Spectrum of the product contains bands attributable to  $Ph-N$ ,  $C=N$  and  $C-F$  which would be present in 3,5-di(pentafluorophenyl)-4-phenyl-1,2,4-triazole, but there is also possibly carbonyl absorption.  $N-H$  or  $CH_3$  groups are not present. The product, therefore, appears to be slightly impure triazole.

(c) Attempted preparation as for the hydrogenic analogue under 1.(a). Phosphorus trichloride (0.96 ml.) was added to a solution of aniline (5.5 ml.) in  $o$ -dichlorobenzene (40 ml.) and the mixture was heated on the steam bath for 30 min.  $N,N'$ -Di(pentafluorobenzoyl)hydrazine (4.2 g.) was added and this mixture was boiled under reflux with stirring for 3 hr. When cold, 2N hydrochloric acid (50 ml.) was added with stirring. The  $o$ -dichlorobenzene layer was separated and evaporated to dryness under reduced pressure. Crystallisation of a portion of the residue from xylene gave colourless prisms, m.p.  $262-267^\circ$ , unchanged on admixture with  $N,N'$ -di(pentafluorobenzoyl)hydrazine. Crystallisation of a portion of the residue from light petroleum/insoluble  $N,N'$ -di(pentafluorobenzoyl)hydrazine was removed from the hot solution by filtration/gave pale yellow prisms, m.p.  $125-146^\circ$ . Comparison of the I.R. spectrum with that of 2,5-di(pentafluorophenyl)-1,2,4-oxadiazole indicates that the impure solid consists chiefly of the oxadiazole.

### Decafluorobenzalazine

A solution of pentafluorobenzaldehyde (18.37 g.) and hydrazone monohydrate (2.28 ml.) in ethanol (50 ml.) was shaken at room temperature for 1 hr. Decafluorobenzalazine (15.5 g.), m.p. 135-136°, crystallised from the solution.

Calc. for  $C_{14}H_2F_{10}N_2$  : C, 43.3; H, 0.52; F, 48.95; N, 7.2.

Found : C, 43.4; H, 0.36; F, 48.8; N, 7.5.

### Attempted preparation of di( $\alpha$ -chloropentafluorobenzylidene)hydrazine

(a) A mixture of N,N'-di(pentafluorobenzoyl)hydrazine (2g.) and phosphorus pentachloride (4 g.) was heated to 140° for 2 hours. The product was dissolved in ether and ice was added. The ether layer was isolated, washed with dilute aqueous sodium bicarbonate and with water and dried ( $MgSO_4$ ). Evaporation of the ether produced a solid which was extracted with hot light petroleum (b.p. 60-80°). When cold, the light petroleum extract gave 2,5-di(pentafluorophenyl)-1,3,4-oxadiazole as colourless needles, m.p. and mixed m.p. 156-158°.

(b) A solution of N,N'-di(pentafluorobenzoyl)hydrazine (1 g.) in thionyl chloride (5 ml.) and N,N-dimethylformamide (0.1 ml.) was boiled under reflux for  $1\frac{1}{2}$  hours, added to ice and the solid (0.85 g.) produced was collected and washed with water. Recrystallisation from light petroleum (b.p. 100-120°) yielded 2,5-di(pentafluorophenyl)-1,3,4-oxadiazole as colourless needles, m.p. and mixed m.p. 155-157°.

(c) Chlorine was passed into a solution of decafluorobenzalazine (1.55 g.) in carbon tetrachloride at room temperature during 3.5 hr. The solid produced by evaporation of the carbon tetrachloride separated from light petroleum (b.p. 100-120°) as yellow needles (1.27 g.), m.p. 135-136°, unchanged on admixture with decafluorobenzalazine. The chlorination was carried out in the absence of direct sunlight and with only dim artificial illumination.

(d) Chlorine was passed into a solution of decafluorobenzalazine (3 g.) in carbon tetrachloride (70 ml.) at room temperature during 3 hr. During the chlorination the solution was irradiated with light from a 250 watt tungsten filament lamp at a distance of 3 cm. The solid produced by evaporation of the carbon tetrachloride was recrystallised from light petroleum (b.p. 60-80°) to give  $\alpha$ -chlorodecafluorobenzalazine (1.9 g.) as yellow prisms, m.p. 85-87°.

Calc. for  $C_{14}HClF_{10}N_2$  : C, 39.8; H, 0.25; Cl, 8.4; F, 44.95; N, 6.65

Found : C, 39.75; H, 0.35; Cl, 9.15; F, 43.6; N, 7.2%

(e) An experiment similar to (b) except that 1 g. of decafluorobenzalazine in 50 ml. of carbon tetrachloride was chlorinated for 6 hr. under irradiation also gave  $\alpha$ -chlorodecafluorobenzalazine.

(f) A solution of decafluorobenzalazine (2 g.) and sulphuryl chloride (1.3 ml.) in carbon tetrachloride (30 ml.) was boiled under reflux with irradiation with light from a 250 watt tungsten filament lamp. No sulphur dioxide or hydrogen chloride was evolved. Benzoyl peroxide (0.12 g.) was added and the mixture was again boiled under reflux with irradiation for 1.5 hr. The solid produced by evaporation of the carbon tetrachloride separated from ethanol as yellow needles (1.48 g.) m.p. 135-136°, unchanged on admixture with decafluorobenzalazine.

Attempted preparation of di( $\alpha$ -bromopentafluorobenzylidene)hydrazine

A solution of decafluorobenzalazine (2 g.) in carbon tetrachloride (20 ml.) was boiled under reflux with N-bromosuccinimide (2 g.) for 17 hr. The insoluble solid, m.p. 170-180° / N-bromosuccinimide, lit. m.p. 174° (ref. 20) <sup>7</sup> was separated from the hot solution by filtration. When cold, the carbon tetrachloride filtrate yielded yellow needles (1.42 g.), m.p. 132-134°, mixed m.p. with decafluorobenzalazine 133-135°.

N-(Pentafluorophenyl)benzenesulphonamide

(a) (Attempted preparation)

A mixture of pentafluoroaniline (9.0 g.) benzene sulphonyl chloride (6.4 ml.) and 2N aqueous sodium hydroxide (60 ml.) was shaken for 2 hr. The pentafluoroaniline initially dissolved in the benzene sulphonyl chloride but slowly crystallised again (m.p. and mixed m.p. 33-35°) as the sulphonyl chloride became hydrolysed by the aqueous solution.

(b) (Attempted preparation)

A solution of pentafluoroaniline (9.15 g.), benzene sulphonyl chloride (6.4 ml.), and N,N-diethylaniline (8.5 ml.) in benzene (100 ml.) was boiled under reflux with stirring for 5 hr. When cold, the solution was washed with 2N hydrochloric acid (2 portions of 50 ml.) and with water and dried ( $MgSO_4$ ). Evaporation of the benzene produced an oil consisting of unchanged benzene sulphonyl chloride and pentafluoroaniline.

- (c) All operations in this preparation up to the addition of water to the reaction mixture were carried out in a nitrogen atmosphere.

n-Butylbromide (3.2 ml.) and ether (50 ml.) was added during 1 hr. to a stirred suspension of finely divided lithium (ca. 1 g.) in ether (50 ml.) at 2-3°. The mixture was stirred at 2° for 30 min. and allowed to warm up to room temperature during 45 min. The solution of lithium butyl was separated from unreacted lithium by filtration through glass wool. The ethereal filtrate was cooled to -60° and pentafluoroaniline (5.17 g.) in tetrahydrofuran (60 ml.) was added with stirring at -60° during 30 min. The mixture was stirred at -60° for 30 min. and benzene sulphonyl chloride (3.65 ml.) in tetrahydrofuran (40 ml.) was added with stirring at -60° during 15 min. After having been stirred at -60° for 30 min. the mixture was allowed to warm up to room temperature during 30 min. and water (85 ml.) and 2N hydrochloric acid (7 ml.) were added. The ethers were removed by distillation and the residue was subjected to steam distillation to remove unchanged pentafluoroaniline and benzene sulphonyl chloride. When cold, a solid crystallised in the distillation residue and this solid was collected and recrystallised from light petroleum to give N-(pentafluorophenyl)-benzenesulphonamide (4 g.) as colourless needles, m.p. 143.5-145°.

Calc. for  $C_{12}H_6F_5NO_2S$  : C, 44.6; H, 1.85; F, 29.4; N, 4.35; S, 9.9

Found : C, 44.85; H, 2.0; F, 32.05; N, 4.65; S, 10.6%

- (d) All operations in this preparation up to the addition of hydrochloric acid/water to the reaction mixture were carried out in a nitrogen atmosphere.

A solution of lithium butyl was prepared from lithium (5 g.), n-butyl bromide (20 ml.) and ether (250 ml.) at -10°. The concentration of the solution was determined titrimetrically. 10 ml. of the solution was added to water and the mixture was titrated against N/10 hydrochloric acid (phenolphthalein indicator) (titre = 71 ml.). 10 ml. of the solution was also added to benzyl chloride (2 ml.) in ether (20 ml.), water (30 ml.) was added, and the mixture was titrated against N/10 hydrochloric acid (phenolphthalein indicator) (titre = 19 ml.). This determination gave the strength of the solution to be 52 mM. of lithium butyl per 100 ml. of solution.

The lithium butyl solution (100 ml.) was added during 1 hr. to a stirred solution of pentafluoroaniline (9.15 g.) in tetrahydrofuran (200 ml.) at -60°. The mixture was stirred at -60° for 1 hr. and benzene sulphonyl chloride (6.4 ml.) in ether (50 ml.) was added with stirring at -60° during

20 min. Stirring was continued whilst allowing to warm up to room temperature during 1 hr. and for 30 min. at 30°. 2N hydrochloric acid (15 ml.) and water (100 ml.) were added, the ethers were removed by distillation and the residue was subjected to steam distillation to remove unchanged pentafluoroaniline and benzene sulphonyl chloride. When cold, a solid (9 g.) crystallised in the distillation residue and this solid was recrystallised from light petroleum (b.p. 100-120°) to give colourless needles (8.8 g.), m.p. 143.5-145°.

3,4,5-Tri(pentafluorophenyl)-1,2,4-triazole

(a) (Attempted preparation)

Phosphorus trichloride (1.0 ml.) was added to a stirred solution of pentafluoroaniline (11 g.) in o-dichlorobenzene (40 ml.) and the mixture was heated on the steam bath for 1 hr. N,N'-Di(pentafluorobenzoyl)hydrazine (4.8 g.) was added and this mixture was boiled under reflux for three hours. N,N'-Di(pentafluorobenzoyl)-hydrazine (1.4 g.), m.p. and mixed m.p. with an authentic specimen 265-267°, separated in the cold and this was collected by filtration. Addition of conc. hydrochloric acid (100 ml.) to the filtrate caused the precipitation of a further quantity of N,N'-di(pentafluorobenzoyl)hydrazine (1.6 g.), m.p. and mixed m.p. 265-267°. The o-dichlorobenzene layer was isolated, washed with conc. hydrochloric acid (100 ml.) and with water and dried (MgSO<sub>4</sub>). Evaporation of the solution gave a solid (1.3 g.) which on recrystallisation from ethanol yielded 2,5-di(pentafluorophenyl)-1,3,4-oxadiazole (1.0 g.) as colourless needles, m.p. and mixed m.p. with an authentic specimen 156-158°.

(b) (Attempted preparation)

3,5-Di(pentafluorophenyl)-1,2,4-triazole (1.303 g.) was dissolved in N/2 aqueous sodium hydroxide (6 ml.) and the water was removed at 100°/0.15 mm. A solution of the salt in pyridine (25 ml.) and hexafluorobenzene (5 ml.) was boiled under reflux for 30 min. and added to an excess of dil. hydrochloric acid. The aqueous layer was decanted from the lower hexafluorobenzene layer and the latter was heated on the steam bath to evaporate solvent. The red solid residue was washed with dil. hydrochloric acid, with 2N aqueous sodium hydroxide and with water. It was insoluble in benzene, ethanol or acetic acid and is possibly, in view of its insolubility, polymeric.



(c) (Attempted preparation)

A mixture of N,N'-di(pentafluorobenzoyl)hydrazine (2.55 g.) pentafluoroaniline (1.8 g.) and phosphorus pentoxide (2 g.) was heated at 210° for 2 hr. then at 250° for 30 min. An excess of water was added and after being kept overnight the insoluble product was extracted with benzene. The solid produced by evaporation of the benzene gave 2,5-di(pentafluorophenyl)-1,3,4-oxadiazole (1.3 g.), m.p. and mixed m.p. 155-157°, on recrystallisation from light petroleum (b.p. 100-120°).

(d) A mixture of N,N'-di(pentafluorobenzoyl)hydrazine (8.4 g.) and N-(pentafluorophenyl)benzenesulphonamide (6.46 g.) was heated at 250-260° for 1 hr. The product was washed thoroughly three times with water at 100°. The aqueous washings were titrated against standard potassium hydroxide (phenolphthalein indicator) and were found to contain 23 mM. of acid (theory for quantitative release of benzene sulphonic acid, 20 mM.). The product insoluble in water was extracted with hot light petroleum (b.p. 100-120°), a petrol-insoluble black solid being removed by filtration. Evaporation of the petrol yielded a brown solid which on recrystallisation from benzene gave the triazole (7.5 g.). Further recrystallisation from benzene, then from ethanol and again from benzene gave colourless prisms, m.p. 180.5-181°.

Anal. Calc. for  $C_{20}F_{15}N_3$  : C, 43.1; H, 0.0; F, 49.35; N, 7.55

Found : C, 42.65; H, 0.0; F, 47.45; N, 7.45%

Calc. M.W. : 567

Found M.W. : 562

Pentafluorobenzhydrazide toluene-p-sulphonate

Toluene-p-sulphonic acid monohydrate (7 g.) was added to a hot solution of pentafluorobenzhydrazide (8.2 g.) in ethanol (60 ml.) and the mixture was boiled under reflux for 2 hours. When cold, the solution deposited colourless plates (11.15 g.), m.p. 226-230° (resolidified and melted again at 238-240°), and addition of ether to the mother liquors precipitated a second crop of the salt (3.2 g.) of similar m.p. The m.p. was unchanged after recrystallisation from methanol/ether.

Calc. for :  $C_{14}H_{11}F_5N_2O_4S$  : C, 42.2; H, 2.8; F, 23.85; N, 7.05; S, 8.05

Found (sample dried 2 hr. at 100°/14 mm.) :

C, 43.0; H, 3.2; F, 22.6; N, 6.9; S, 7.85

3,5-Di(pentafluorophenyl)-1,2,4-triazole

(a) (Attempted preparation)

A mixture of pentafluorobenzhydrazide (0.56 g.) and pentafluorobenzonitrile (4 ml.) was heated to 230° for 2 hours in a glass tube, which had been sealed under vacuum. The excess of pentafluorobenzonitrile was removed by distillation under reduced pressure and the residue, a black pitch, was extracted with dilute aqueous sodium hydroxide. Addition of hydrochloric acid to the alkaline extract produced a solid, m.p. 150-200°, from which no pure compound was isolated after recrystallisation from a variety of solvents.

(b) A mixture of pentafluorobenzhydrazide toluene-p-sulphonate (11.1 g.) and pentafluorobenzonitrile (7 ml.) was boiled under reflux for 3 hours. The excess of pentafluorobenzonitrile was removed by distillation under reduced pressure and the residue was extracted several times with dilute aqueous sodium hydroxide. Acidification of the alkaline extracts with hydrochloric acid produced a solid which was recrystallised twice from light petroleum (b.p. 100-120°) (charcoal) to yield 3,5-di(pentafluorophenyl)-1,2,4-triazole (2.9 g.) as colourless prisms, m.p. 216-218°.

Calc. for  $C_{14}H_2F_{10}N_3$  : C, 41.9; H, 0.25; F, 47.35; N, 10.5

Found : C, 42.1; H, 0.28; F, 47.3; N, 10.6

Attempted Preparation of 3,3'-p-phenylenebis-(5-phenyl-1,2,4-triazole).

Toluene-p-sulphonic acid monohydrate (18 g.) was added to a hot solution of benzhydrazide (13.6 g.) in ethanol (30 ml.) and the mixture was boiled under reflux for 1 hour. Colourless needles separated in the cold and this product was collected by filtration and was recrystallised from ethanol/ether to yield colourless needles, (15 g.), m.p. 153-154°, of benzhydrazide toluene-p-sulphonate.

Calc. for  $C_{14}H_{16}N_2O_4S$  : C, 54.55; H, 5.25; N, 9.1; S, 10.4

Found (sample dried 1 hr. at 100°/0.2 mm.)

C, 54.6; H, 5.1; N, 9.25; S, 10.35, 10.25

The analytical figures indicate that the product is the anhydrous salt. Potts (ref. 21) reported a m.p. 205° for the monohydrate.

A mixture of benzhydrazide toluene-p-sulphonate (5 g.) and p-dicyanobenzene (1 g.) was heated to 237° for 3 hours. When cold, the product was extracted with 2N aqueous sodium hydroxide and the alkaline extract was acidified with hydrochloric acid. The precipitated solid had an indefinite m.p. (140-200°) and no pure product was isolated after recrystallisation from a variety of solvents.

Attempted preparation of perfluorinated arylimino ether hydrochlorides

**Ethyl pentafluorobenzimino ether hydrochloride**

Hydrogen chloride was passed into a solution of pentafluorobenzonitrile (4.8 g.) and anhydrous ethanol (1.45 ml.) in anhydrous ether (5 ml.) at room temperature, during 2 hours. No crystals separated on standing overnight. The ether was distilled off at room temperature under reduced pressure to give an oil with an odour similar to that of the starting nitrile. On long standing a very few crystals, m.p. 143-8° separated. There was insufficient of this solid for recrystallisation, and hence for analysis. Aspects of the infra-red spectrum were not inconsistent with those expected for the required product, although most of the bands could not be assigned.

**Phenyl pentafluorobenzimino ether hydrochloride**

(a) Hydrogen chloride was passed into a solution of pentafluorobenzonitrile (3.24 g.) and phenol (1.58 g.) in ether (20 ml.) at room temperature during 1 hour. No solid separated after three weeks at room temperature.

(b) An experiment similar to (a) except that benzene (20 ml.) was used as solvent in place of ether gave no solid. The benzene solution was subsequently treated with hydrogen chloride at the boiling point but again no solid separated.

**Diethyl tetrafluoro-p-phenylene tetrafluoroterephthalimino ether dihydrochloride**

Hydrogen chloride was passed during 2 hours into a solution of tetrafluoroterephthalonitrile (2 g.) in anhydrous dioxan (10 ml.) containing anhydrous ethanol (0.57 ml.) at 80-85°. On cooling, the nitrile (1.6 g.), m.p. 197-9° separated.

### Tetrafluoroterephthalaldihydrazide

(a) From Dimethyl tetrafluoroterephthalate and Hydrazine (ref. 1)

The compound, m.p. 253° (decomp.) from dimethyl tetrafluoroterephthalate and aqueous hydrazine gave an unsatisfactory elemental analysis

Calc. for  $C_8H_6F_4N_4O_2$  : C, 36.1; H, 2.3; F, 28.6; N, 21.1

(1) Found : C, 38.6; H, 3.5; F, 30.9; N, 20.3 (analysis, ref. 1)

(2) Found : C, 36.8; H, 2.4; F, 29.1; N, 21.7 (repeat analysis)

(b) From Tetrafluoroterephthaloyl chloride and Hydrazine

Tetrafluoroterephthaloyl chloride (9.0 g.; ref. 1) in anhydrous ether (150 ml.) was added at -2° to 5°, over 40 min., to a well stirred mixture of 95% hydrazine (4.4 ml.) in anhydrous ether (200 ml.) When the addition was complete the mixture was allowed to rise to room temperature (ca. 45 min.) and was stirred at room temperature for 30 min. The solid collected by filtration was boiled with water (500 ml.) and the hot solution was filtered from insolubles (1.0 g., m.p. >400°). On cooling there were obtained off-white crystals (5.1 g.), m.p. 245.5-246° (decomp.). Recrystallisation from 2-ethoxyethanol yielded tetrafluoroterephthalaldihydrazide (2.7 g.), m.p. 247.5-248° (decomp.), and the mother liquors yielded a further quantity (0.5 g.), m.p. 245-245.5°, and crude material (m.p. 240°) by full evaporation of the solvent.

In a subsequent preparation using tetrafluoroterephthaloyl chloride (13.5 g.), the solid obtained by filtration of the reaction mixture was washed with water (150 ml.) and was then extracted three times with boiling water. When cold the extracts yielded tetrafluoroterephthalaldihydrazide (7.5 g.), m.p. 246-248° (decomp.), and, after partial evaporation, a second crop (0.56 g.), m.p. 243-246° (decomp.).

### Tetrafluoroisophthaloyl bis(pentafluorobenzhydrazide)

(a) (Attempted preparation via tetrafluoroisophthaloyl bishydrazide)

Tetrafluoroisophthaloyl chloride (7.9 g.) in anhyd. ether (130 ml.) was added to a well stirred mixture of anhyd. hydrazine (3.86 ml. assumed 95%  $N_2H_4$ ) in anhyd. ether below 5°. The mixture was stirred, allowing to rise to room temperature and was kept overnight. The off-white solid was

collected by filtration (leaving brown resin on the sides of the flask) and was washed with ether and water to give a residue (2.0 g.) m.p. >400°. Hence this product, insoluble in water, is probably polymeric. It is possible that some of the required product was formed but was lost on washing with water.

(b) The di-acid chloride (5.75 g.) in anhyd. benzene (25 ml.) was added to a stirred and refluxing solution of pentafluorobenzhydrazide (9.5 g.) in anhyd. benzene (150 ml.), followed by N,N-diethylaniline (7.0 ml.) in anhyd. benzene (25 ml.) over 3 min. The mixture was stirred under reflux for 75 min. and was cooled, and filtered. The white solid collected retained a large amount of benzene and was washed with petrol, dried, triturated with dilute hydrochloric acid, washed acid-free, and dried. This crude product (12.85 g.) was recrystallised from a mixture of ethanol (400 ml.) and water (200 ml.) to yield the bis(benzhydrazide) (8.0 g.), m.p. >400°. A sample was recrystallised for analysis.

Calc. for  $C_{22}H_4F_4N_4O_4$  : C, 40.4; H, 0.62; F, 40.6; N, 8.6

Found : C, 40.5; H, 0.47; F, 40.8; N, 8.4

Tetrafluoroterephthaloyl bis(pentafluorobenzhydrazide)

(a) Tetrafluoroterephthaloyl chloride (0.55 g.) in anhydrous benzene (5 ml.) was added to a stirred solution of pentafluorobenzhydrazide (1.0 g.) dissolved in anhydrous benzene (25 ml.), followed by a solution of N,N-diethylaniline (0.71 ml.) in anhydrous benzene (5 ml.) during 10 min. The mixture was stirred under reflux during 80 min. and was filtered hot. The collected solid (1.3 g.) was washed with benzene, dried, and triturated with water to yield the product (1.1 g.), m.p. >300°. Recrystallisation from aqueous pyridine gave crystals, m.p. >370°.

(b) Pentafluorobenzoyl chloride (4.55 g.) in anhydrous benzene (5 ml.) was added to tetrafluoroterephthalaldihydrazide (2.55 g.) suspended in anhydrous benzene (150 ml.) with stirring under reflux. N,N-Diethylaniline (3.25 ml.) in anhydrous benzene (5 ml.) was added over 10 min. and the mixture was stirred under reflux during 3 hours. The solid was collected by filtration, washed with benzene, sucked dry, triturated with water, and the product (5.65 g.), m.p. >400°, was collected by filtration and washed with water.

The products prepared by methods (a) and (b) had identical infrared spectra observed over 2-15  $\mu$ .

p-Di(2-pentafluorophenyl-1,3,4-oxadiazolyl-5)tetrafluorobenzene

Tetrafluoroterephthaloyl bis(pentafluorobenzhydrazide) (1 g.) and phosphoryl chloride (25 ml.) were stirred on the steam bath during 17 hours. The excess of phosphoryl chloride was distilled off in vacuo and the residual gum was treated with ethanol. Foaming occurred with evolution of hydrogen chloride and the buff solid formed was filtered off, washed with ethanol and ether and dried. The crude product (0.76 g.), m.p. 290-1°, was recrystallised twice from xylene to yield the required bisoxadiazole (0.5 g.), m.p. 290.5-291.5°.

Calc. for  $C_{22}F_{14}N_4O_2$  : C, 42.7; H, 0.00; F, 43.0; N, 9.1

Found : C, 42.9; H, 0.05; F, 42.85; N, 9.1

m-Di(2-pentafluorophenyl-1,3,4-oxadiazolyl-5)tetrafluorobenzene

Tetrafluoroisophthaloyl bis(pentafluorobenzhydrazide) (5.0 g.) and phosphorus oxychloride (125 ml.) were stirred on the steam bath during 18 hr. The excess of phosphorus oxychloride was distilled off, to the residue was added ice, and the suspension was filtered. The white solid collected was washed free of acid to yield the crude product (4.6 g.), m.p. 189-193°. Recrystallisation first from 2-ethoxyethanol and then from petrol/benzene yielded the bis(oxadiazole) (2.8 g.), m.p. 194.5-195.5°. A sample was recrystallised from petrol (b.p. 100-120°) for analysis : the m.p. was unchanged.

Calc. for  $C_{22}F_{14}N_4O_2$  : C, 42.7; H, 0.00; F, 43.0; N, 9.1

Found : C, 42.9; H, 0.00; F, 42.8; N, 9.1

Attempted preparation of m-Di(2-pentafluorophenyl-1,3,4-thiadiazolyl-5)tetrafluorobenzene

The bis(oxadiazole) (0.5 g.), phosphorus pentasulphide (0.5 g.), and sym.-tetrachloro-ethane (40 ml.) were stirred under reflux during 4½ hr., the mixture becoming red. The cooled mixture was filtered from high melting solid (0.2 g.), m.p. 277°, probably a reaction product of the solvent with phosphorus pentasulphide. The filtrates gave crystals (0.2 g.) on standing, which recrystallised from petrol (100-120°) had m.p. 194-5°. Removal of the solvent from the mother liquors by distillation gave a dark brown residue, m.p. 180-195°. Both crystals and residue had an undepressed m.p. when mixed with the bis(oxadiazole). The infra-red spectrum of the crystals was identical with that of the bis(oxadiazole).

Attempted Preparation of p-Di(2-pentafluorophenyl-1,3,4-thiadiazolyl-5)tetrafluorobenzene

(a) p-Di(2-pentafluorophenyl-1,3,4-oxadiazolyl-5)tetrafluorobenzene (0.5 g. ref. 4), phosphorus pentasulphide (0.5 g.) and sym.-tetrachloroethane (40 ml.) were stirred under reflux during 48 hr. The hot solution was decanted from dark solid, and the solution was cooled and filtered. The solid collected was recrystallised from 2-ethoxyethanol, m.p. 290-5°, and the mixed m.p. with the starting material (m.p. 290-290.5°) was 291-2°.

(b) Tetrafluoroterephthaloyl bis(pentafluorobenzyhydrazide) (1.0 g.; ref. 4), phosphorus pentasulphide (1.0 g.), and sym.-tetrachloroethane (75 ml.) were stirred under reflux during 48 hr. The hot mixture was filtered and the trace of dark solid collected was discarded. The filtrates yielded crystals (0.5 g.) which were collected by filtration, washed with the solvent and petrol (b.p. 40-60°), m.p. indef. Recrystallisation from benzene and from 2-ethoxyethanol gave material of indefinite m.p., softening at 233°. This product had no CO or NH absorption in the infra-red spectrum. Hence it is not the starting material, and cyclisation would seem to have occurred.

Attempted preparation of 2,2'-di(pentafluorophenyl)-5,5'-di(trifluorobenzimidazole)

(a) Via Phenyl pentafluorobenzoate

A solution of pentafluorobenzoyl chloride (9.22 g.), phenol (3.76 g.), and N,N-diethylaniline (6.5 ml.) in benzene (50 ml.) was boiled under reflux with stirring for 2 hr. Benzene (50 ml.) was added and the benzene solution was washed twice with dil. hydrochloric acid and once with water and was dried (MgSO<sub>4</sub>). Evaporation of the benzene gave a solid which separated from aqueous ethanol as colourless needles (8.5 g.), m.p. 68°.

Calc. for C<sub>13</sub>H<sub>5</sub>F<sub>5</sub>O<sub>2</sub> : C, 54.2; H, 1.75; F, 32.95

Found : C, 54.1; H, 2.1; F, 34.1%

A mixture of 3,3',4,4'-tetraaminohexafluorobiphenyl (5.25 g.) and phenyl pentafluorobenzoate (8.44 g.) was heated under reflux under nitrogen at 300° for 2 hr. The ester continued to reflux during the whole of that period and some distilled out of the reaction mixture. Acidic vapours, probably hydrogen fluoride, were evolved during the reaction. The product was washed successively with water, benzene, ether, and ethanol to yield a black solid (5 g.) insoluble in common organic solvents or in conc. acid or alkali, m.p. >400°. No useful information could be obtained from the I.R. spectrum of the solid. Evaporation of the benzene and ether washings yielded phenyl pentafluorobenzoate (4.8 g.), m.p. 61-68°.

(b) Via the di(pentafluorobenzoyl) derivative of tetraaminohexafluorobiphenyl

3,3',4,4'-Tetraaminohexafluorobiphenyl (3.22 g.), pentafluorobenzoyl chloride (4.61 g.), N,N-diethylaniline (3.5 ml.) and benzene (50 ml.) were boiled under reflux with stirring for 6.5 hr. When cold, 2N hydrochloric acid (50 ml.) was added and the mixture was stirred for 10 min. The benzene and aqueous layers were decanted from the product, which was a brown gum. The gum was finally dried at 60°/0.15 mm. for 2 hr.

A portion of the gummy product was heated at 300° for 2.5 hr. Recrystallisation from aqueous acetic acid yielded a solid of indefinite m.p. Further recrystallisation did not produce a pure compound.

(c) 3,3',4,4'-Tetraaminohexafluorobiphenyl (3.22 g.), pentafluorobenzoic acid (4.24 g.) and polyphosphoric acid (ca. 80% P<sub>2</sub>O<sub>5</sub>) (30 ml.) were stirred at 175° for 4 hr., allowed to cool to 100° and poured into water. A black solid was precipitated and this was collected by filtration, dissolved in very dilute sodium hydroxide and reprecipitated by the addition of hydrochloric acid. The product, m.p. 160-190°, was soluble in ethanol, acetic acid or dilute aqueous sodium hydroxide, sparingly soluble in hot xylene, and insoluble in water or hydrochloric acid. The infra-red spectrum of the product had bands at 2.9-4 $\mu$ , 6.05 $\mu$  and 6.6-6.7 $\mu$ , which are all indicative of the presence of  $\begin{array}{c} \text{--C--N--H} \\ \parallel \\ \text{O} \end{array}$ . Therefore, cyclisation to the imidazole

structure does not appear to have taken place. Attempts to purify the black product have so far been unsuccessful.

(d) A reaction similar to (c), except that a reaction temperature of 250° instead of 175° was used, gave a similar product.

### 3. AMIDES

#### Tetrafluoroisophthaldi(pentafluoroanilide)

A mixture of tetrafluoroisophthaloyl chloride (5.5 g.), pentafluoroaniline (7.32 g.), N,N-diethylaniline (7 ml.) and benzene (60 ml.) was boiled under reflux with stirring for 5 hours. When cold, the product was shaken with N/1 hydrochloric acid (50 ml.) and the solid which was precipitated was collected and washed with water and with benzene. Recrystallisation from aqueous ethanol gave the anilide (9 g.) as colourless prisms, m.p. 323-325° (decomp.).

Calc. for C<sub>20</sub>H<sub>2</sub>F<sub>14</sub>N<sub>2</sub>O<sub>2</sub> : C, 42.3; H, 0.35; F, 46.8; N, 4.95

Found : C, 42.2; H, 0.5; F, 46.95; N, 5.0%



Tetrafluoroterephthaldi(pentafluoroanilide)

The preparation of this anilide has been reported previously (ref. 1) and further analytical figures are now available.

Calc. for  $C_{20}H_2F_{14}N_2O_2$  : C, 42.3; H, 0.35; N, 4.95

Found : C, 42.05; H, 0.9; N, 5.4%

m- and p-Di(pentafluorobenzamido)tetrafluorobenzene

A mixture of tetrafluoro-m-phenylenediamine (3.6 g.) (ref. 1), pentafluorobenzoyl chloride (9.22 g.), N,N-diethylaniline (7 ml.) and benzene (50 ml.) was boiled under reflux with stirring for 5 hours. When cold, benzene (100 ml.) and 2N hydrochloric acid (250 ml.) were added and the mixture was stirred for 15 min. The solid which had been precipitated was collected by filtration and washed with water. The solid was only partially soluble in acetone, and the solid (a) produced by evaporation of an acetone extract was recrystallised from aqueous ethanol to give 1,3-di(pentafluorobenzamido)tetrafluorobenzene (6 g.) as colourless prisms, m.p. 298-300° (decomp.).

Calc. for  $C_{20}H_2F_{14}N_2O_2$  : C, 42.3; H, 0.35; F, 46.8; N, 4.95

Found : C, 42.3, 42.85; H, 0.35, 0.47; F, 46.6, 40.8; N, 5.05%

A second crop of impure material (1.8 g.), m.p. 270-296°, was obtained after concentration of the aqueous ethanolic mother liquors.

The solid (b; 1 g.) which was insoluble in acetone separated from ethanol/N,N-dimethylformamide as colourless prisms, m.p. 353.5-355.5° (decomp.).

Calc. for  $C_{20}H_2F_{14}N_2O_2$  : C, 42.3; H, 0.35; F, 46.8; N, 4.95

Found : C, 42.3; H, 0.10; F, 46.9; N, 5.0.

Tetrafluoro-p-phenylene diamine (1.85 g.), N,N-diethylaniline (3.5 ml.), and pentafluorobenzoyl chloride (4.75 g.) in benzene (40 ml.) were boiled under reflux during 5 hr. 2N Hydrochloric acid was added and the product was collected by filtration, washed with water and with acetone. Recrystallisation from ethanol/dimethylformamide gave 1,4-di(pentafluorobenzamido)tetrafluorobenzene as colourless prisms (3.7 g.), m.p. 353.5-355.5° (decomp.). This compound and the side-product (b) had identical infra-red spectra. Hence the tetrafluoro-m-phenylene diamine contains ca. 10% of the p-isomer (see also under IMIDES).

#### N,N,N',N'-Tetraphenylphthaldiamide

A mixture of phthaloyl chloride (21 g.), diphenylamine (33 g.), N,N-diethylaniline (37 ml.) and benzene (150 ml.) was boiled under reflux with stirring for 6 hours. When cold, the solid (39 g.) was collected by filtration and was washed with benzene and with water. Two recrystallisations from benzene/ethanol gave colourless prisms, m.p. 243-245°/lit. m.p. 238-238.5° (ref. 8)7.

#### N,N,N',N'-Tetraphenylterephthaldiamide

A mixture of terephthaloyl chloride (21 g.), diphenylamine (33 g.), N,N-diethylaniline (37 ml.) and benzene (150 ml.) was boiled under reflux with stirring for 5 hours. When cold, the solid (49 g.) was collected by filtration and washed with water.

Two recrystallisations from light petroleum (b.p. 100-120°) gave colourless prisms, m.p. 280-282°/lit. m.p. 272-273° (ref. 9)7.

#### N,N'-Dibenzoyl-N,N'-diphenyl-p-phenylenediamine

A mixture of benzoyl chloride (5.9 ml.), N,N'-diphenyl-p-phenylenediamine (6.5 g.)/purified by two recrystallisations from light petroleum (b.p. 100-120°)7, N,N-diethylaniline (8.4 ml.) and benzene (100 ml.) was boiled under reflux with stirring for 7 hours. The solution was evaporated to dryness and the residue was washed well with water. Recrystallisation from benzene/light petroleum (b.p. 80-100°) gave colourless prisms (8 g.), m.p. 228-230°/lit. m.p. 218.5° (ref. 10)7.

#### Attempted preparation of N,N,N',N'-tetra(pentafluorophenyl)-terephthaldiamide

A mixture of terephthaloyl chloride (1.0 g.), decafluorodiphenylamine (3.22 g.), and pyridine (25 ml.) was boiled under reflux with stirring for 1.5 hr. The solid which was precipitated on adding to an excess of water was collected, washed with water and extracted with hot light petroleum (b.p. 100-120°). When cold, the partially evaporated extract yielded a solid, m.p. 175-230°. Further recrystallisation of the product did not yield a compound with a narrow melting range.

N,N,N',N'-Tetra(pentafluorophenyl)tetrafluoroterephthaldiamide

(a) (Attempted Preparation)

A solution of tetrafluoroterephthaloyl chloride (2.35 g.), decafluorodiphenylamine (5.96 g.), and N,N-diethylaniline (3 ml.) in benzene (50 ml.) was boiled under reflux with stirring for 5 hr. When cold, the solution was diluted with benzene (50 ml.), washed with 2N hydrochloric acid (2 portions of 25 ml.) and with water (2 portions of 50 ml.) and dried (MgSO<sub>4</sub>). The residue remaining after evaporation of the benzene was shaken for 1 hr. with 2N aqueous sodium hydroxide (50 ml.) and ethanol (2 ml.) and the crystalline solid obtained was collected and washed with water. This product was unchanged decafluorodiphenylamine (5.54 g.), m.p. 81-83°, mixed m.p. 81-83.5°.

(b) All operations in this preparation up to the addition of water to the reaction mixture were carried out in a nitrogen atmosphere.

n-Butyl bromide (2.4 ml.) in ether (40 ml.) was added during 45 min. to a stirred suspension of finely divided lithium (ca. 1 g.) in ether (65 ml.) at 5-10°. The mixture was stirred at 5° for 30 min. and allowed to warm up to room temperature during 1.5 hr. The solution of lithium butyl was separated from unreacted lithium by filtration through glass wool. The ethereal filtrate was cooled to -60° and decafluorodiphenylamine (6.98 g.) in tetrahydrofuran (50 ml.) was added with stirring at -60° during 30 min. The mixture was stirred at -60° for 30 min. and tetrafluoroterephthaloyl chloride (2.75 g.) in tetrahydrofuran (60 ml.) was added with stirring at -60° during 15 min. After having been stirred at -60° for 15 min., the mixture was allowed to warm up to room temperature during 30 min. and water (3 ml.) and 2N hydrochloric acid (1 ml.) were added. The product (8 g.), which was insoluble in the reaction mixture, was collected by filtration and washed with ether. A portion (7 g.) of the product was recrystallised from N,N-dimethylformamide, then from xylene and was washed with water, ethanol and ether. A final recrystallisation from methyl ethyl ketone gave N,N,N',N'-tetra(pentafluorophenyl)tetrafluoroterephthalamide (2.1 g.) as colourless prisms, m.p. 291-292°.

Anal. Calc. for C<sub>32</sub>F<sub>24</sub>N<sub>2</sub>O<sub>2</sub> : C, 42.7; H, 0.0; F, 50.65; N, 3.1;

Found : C, 43.2, 42.35; H, 0.4, 0.15; F, 42.5; N, 3.2%

#### 4. IMIDES

##### m-Di(tetrafluorophthalimido)tetrafluorobenzene

The preparation of the tetrafluoro-m-phenylene diamine has been already reported (ref. 1).

The diamine (1.2 g.) and N,N-diethylaniline (4.3 ml.) in anhydrous benzene (30 ml.) were added during 60 min. to a stirred and refluxing solution of tetrafluorophthaloyl chloride (3.7 g.) in anhydrous benzene (30 ml.) with the momentary formation of an intense orange colour as the solutions mixed. Gradually the mixture became yellow and gave a precipitate. The mixture was stirred under reflux during 1 hr. and the precipitate was collected by filtration, washed free of yellow colour with benzene, and dried. Hydrochloride of N,N-diethylaniline was removed by trituration with water and the residue (3.4 g.) was recrystallised from 2-ethoxyethanol to give the product (A) (2.6 g.), m.p. 292-292.5°, and an insoluble fraction (B) (0.2 g.), m.p. >400°. The infra-red spectra of both of these products were very similar, with no NH absorption. A further product (C) (0.3 g.), m.p. 346.5-347.5°, from aqueous acetic acid, was isolated from the benzene filtrates of the reaction mixture. The infra-red spectrum of (C) was also very similar to the spectra of (A) and (B), and with no NH absorption. For further discussion concerning these products see under p-di(tetrafluorophthalamido)tetrafluorobenzene, below.

Anal. Calc. for  $C_{22}F_{12}N_2O_4$  : C, 45.2; H, 0.00; F, 39.0; N, 4.8

Found for (A): C, 44.9; H, 0.00; F, 35.7; N, 4.5

Found for (C): C, 45.8, 45.5; H, 0.00, 0.56; F, 32.7, 38.9; N, 5.0.

##### p-Di(tetrafluorophthalimido)tetrafluorobenzene

(a) Tetrafluorophthalic anhydride (0.55 g.), tetrafluoro-p-phenylenediamine (0.2 g.) and acetic acid (5 ml.) were boiled under reflux for 2 hr. A solid (0.2 g.) which crystallised from the hot solution, was collected by filtration and recrystallised from N,N-dimethylformamide to give yellow needles, m.p. >430°.

Anal. Calc. for  $C_{22}F_{12}N_2O_4$  : C, 45.25; H, 0.0; F, 39.05; N, 4.8

Found : C, 45.9; H, 0.2 ; F, 36.2; N, 5.45%

The acetic acid mother liquors were evaporated to dryness and the residue was recrystallised from aqueous 2-ethoxyethanol to give colourless needles, m.p. 209-212°. This product has  $NH_2$  absorption in the infra-red and it is probably 4-(tetrafluorophthalimido)tetrafluoroaniline.

Anal. Calc. for  $C_{14}H_2F_8N_2O_2$  : C, 44.0; H, 0.55; F, 39.75; N, 7.35

Found : C, 44.2; H, 0.15; F, 39.8; N, 7.2%

(b) A solution of tetrafluoro-*p*-phenylenediamine (0.6 g.) and *N,N*-diethylaniline (2.5 ml.) in benzene (20 ml.) was added to tetrafluorophthaloyl chloride (1.84 g.) in benzene (30 ml.) and the mixture was boiled under reflux with stirring for 5 hr. When cold, 2*N* hydrochloric acid (20 ml.) was added, and an insoluble solid (1.32 g.) was collected by filtration and washed with benzene, dil. hydrochloric acid, water, ethanol, and ether. Recrystallisation from *N*-methylpyrrolidone gave pale yellow needles, m.p. >516°.

Anal. Calc. for  $C_{22}F_{12}N_2O_4$  : C, 45.25; H, 0.0; F, 39.05; N, 4.8

Found : C, 44.45; H, 0.55; F, 49.55; N, 5.2%

The product from (b) has an infra-red spectrum which is very similar to that of the product of m.p. >430° from (a) and also to that of the compound (B) of m.p. >400° obtained as a side product from the reaction of impure tetrafluoro-*m*-phenylenediamine with tetrafluorophthaloyl chloride (above). The last two spectra contained extra weak bands, probably due to impurities.

The isolation of *p*-di(pentafluorobenzamidò)tetrafluorobenzene from the reaction of pentafluorobenzoyl chloride with a sample of the same tetrafluoro-*m*-phenylene diamine (see under AMIDES) shows that this *m*-diamine contains at least 10% of the *p*-isomer. Although the diamine was originally thought to be of 97% purity (ref. 1), further analysis by gas chromatography using different conditions has shown that the *m*-diamine contains both the ortho and para isomers as impurities. Hence compound (C) obtained as a side-product in the tetrafluorophthalimidation of the impure tetrafluoro-*m*-phenylene diamine could be *o*-di(tetrafluorophthalimido)tetrafluorobenzene.

Employing a six foot column of 10% Versamide 900 deposited on Embacel with a flow of helium at 80 ml./min., programmed over 100-120° rising at 7.5°/min., and a katherometer detector, the following compounds were eluted (the percentages are only approximate, being based on approximate area ratios) in the order given, from the tetrafluoro-*m*-phenylene diamine :

- |   |         |
|---|---------|
| 1. Pentafluoroaniline                       | ca. 1%  |
| 2. Tetrafluoro- <i>p</i> -phenylene diamine | ca. 15% |
| 3. Tetrafluoro- <i>m</i> -phenylene diamine | ca. 85% |
| 4. Tetrafluoro- <i>o</i> -phenylene diamine | ca. 5%  |

Compounds 1, 2, and 4 were available as reference samples.

## 5. CARBONATES AND CHLOROFORMATES

### Pentafluorophenyl Chloroformate

The spectrum of this compound (ref. 1) as prepared earlier had hydroxyl absorption. Prepared as described below, there was very little hydroxyl absorption.

Pentafluorophenol (50.3 g.), N,N-diethylaniline (43.7 g.), and anhydrous ether (85 ml.) were added over  $4\frac{1}{2}$  hr. to a stirred solution of phosgene (85 g.) in anhydrous ether (260 ml.) at 0-5°. Diethylaniline hydrochloride was filtered off and phosgene and ether were distilled off. The fore-fraction (2.2 g.), b.p. 52-3°/13 mm. was discarded and the main fraction (43.5 g.), b.p. 53°/13 mm. was collected. A fraction (7.2 g.), b.p. 131-2°/13 mm., solidified and was recrystallised from petrol. This is probably di(pentafluorophenyl)carbonate, m.p. 50-52°, from the elemental analysis :

Calc. for  $C_{13}F_{10}O_3$  : C, 39.6; F, 48.2%

Found : C, 39.8; F, 47.6%

### Di(pentafluorophenyl)tetrafluoro-m-phenylene biscarbonate

Tetrafluororesorcinol (4.0 g.) in benzene (160 ml.) was azeotropically dried, the benzene which was removed by distillation being replaced by anhydrous benzene. To the stirred and refluxing solution was added pentafluorophenyl chloroformate (11.2 g.) during a few minutes, and N,N-diethylaniline (7.2 ml.) was added dropwise during 20 min. The solution now turbid, became clear on refluxing for 1 hr. When cool crystals of diethylaniline hydrochloride separated, and the mother liquors were distilled to dryness. Recrystallisation of a sample of the residue from petrol (b.p. 40-60°) gave product of m.p. 74-85°. The whole of the product was distilled to give solid (6.35 g.), b.p. 160-2°/0.25 mm., m.p. 89.5-91°. Three recrystallisations from petrol (b.p. 60-80°) yielded the biscarbonate (3.3 g.), m.p. 101-2°. No absorption due to hydroxyl was observed in the infra-red spectrum of this product.

Calc. for  $C_{20}F_{14}O_6$  : C, 39.9; F, 44.1

Found : C, 40.4, 40.15; H, 0.05, 0.13; F, 38.6, 42.0, 40.4.

Di(pentafluorophenyl)octafluoro-4,4'-biphenylene biscarbonate

Octafluoro-4,4'-dihydroxybiphenyl (6.0 g.) and pentafluorophenyl chloroformate (15.0 g.) were heated at 150-160° (bath) for 6½ hr. The mixture set to a crystalline mass when cold and the whole was recrystallised from petrol (b.p. 60-80°) to yield crystals (7.2 g.), m.p. 115-122°. Three recrystallisations raised the m.p. to 125-6°.

Calc. for  $C_{26}F_{18}O_6$  : C, 41.6; H, 0.0; F, 45.6

Found : C, 41.4; H, 0.1; F, 41.0, 39.3, 41.4.

Di(pentafluorophenyl)tetrafluoro-p-phenylene biscarbonate

Tetrafluorohydroquinone (1.66 g.) in benzene (190 ml.) was azeotropically dried. Pentafluorophenyl chloroformate (4.65 g.) was added over 2 min., followed by N,N-diethylaniline (3.0 ml.), added over 20 mins. to the stirred and refluxing solution. The mixture, now containing a white precipitate of the amine hydrochloride, was stirred under reflux during 1 hr. and filtered. The filtrates were washed with dilute hydrochloric acid, washed free of acid with water, and dried ( $MgSO_4$ ). Removal of the solvent by distillation yielded an oil which rapidly solidified. Distillation of this crude product, m.p. 123-133°, gave a fore-fraction, b.p. 131-156°/0.3 mm, and a main fraction (4.1 g.), b.p. 162-4°/0.3 mm., m.p. 133-8°. Three recrystallisations from petrol (b.p. 60-80°) successively gave melting points 129-131°, 131-132°, 129.5-131°. As the compound could not be obtained pure it was not submitted for analysis. Other attempts to prepare this compound have been described previously (ref. 1). In the present product no hydroxyl could be found in the infra-red spectrum.

Diphenyl p-phenylene biscarbonate (IX)

When the earlier preparation of the carbonate (ref. 1) was heated at 250° in a soda glass tube, it solidified over 10 min. The solidified material was allowed to cool and was extracted from the tube, crushed, triturated with ether and boiled with petrol (b.p. 100-120°) to extract any low molecular weight reaction products or starting material. A small quantity of the latter, m.p. 175-180°, separated from the petrol extract. The majority of the solid did not dissolve and was found to have a spectrum substantially the same as that of the starting material, despite the fact that no melting point was observed up to 400°. Hence, this solid is probably a polycarbonate (cf. ref. 12). The ethereal extract on partial evaporation gave white solid, m.p. 65°, in very small amount, which, when recrystallised

from petrol (b.p. 60-80°), had m.p. 77-9° and an infra-red spectrum identical with that of diphenyl carbonate (lit. m.p. 78° and 88°).

It was also found that a definite melting point could be obtained for the earlier preparation of this compound, if the melting point sample was not in contact with soda glass. In a Pyrex capillary, the melting point 175-7° was obtained, whereas the melting point had previously (ref. 1) been reported as indeterminate (ca. 168°), accompanied by re-solidification of the melt in a soda glass capillary.

This compound was re-prepared as described earlier (ref. 1) but on twice that scale. The crude product (7.9 g.), m.p. 171-6°, recrystallised from petrol to give impure material (6.9 g.), m.p. 171-7°, and was distilled, but only a small fraction, b.p. 220-230°/0.2 mm. of lower m.p. was obtained and most of the product solidified in the still on further heating. This distillation was only attempted after it had been shown that a sample of the earlier preparation appeared to be stable when heated in a Pyrex tube at 250° during 1½ hr.

#### Diphenyl 4,4'-biphenylene biscarbonate (X)

A sample of the earlier (ref. 1) preparation was heated in a Pyrex tube at 250° during 1½ hr. without the melt solidifying. However, when a sample in a soda glass tube was inserted in a bath at 250° there was almost immediate solidification. The material was allowed to cool and was extracted from the tube, crushed, triturated with ether followed by ethanol, and the residue was boiled with petrol. The ethereal solution on partial evaporation gave a solid of indefinite m.p. which when recrystallised from petrol (b.p. 100-120°) had m.p. 161-5°, undepressed mixed with the starting material. The insoluble material remaining from the extractions had an infra-red spectrum substantially the same as that of the starting material. This, coupled with the lack of a melting point below 400° suggests that the product is a polycarbonate (cf. ref. 12).

This carbonate was re-prepared as described earlier (ref. 1) but on twice that scale. The crude product (15.1 g.) was recrystallised from benzene/petrol to give impure material (10.9 g.), m.p. 164-170°. A second recrystallisation from benzene/petrol did not raise the m.p. Two recrystallisations of a sample from isopropanol gave product of m.p. 171-5°. The remainder (8.0 g.) was distilled from a pear-shaped Claisen flask to yield the biscarbonate (5.9 g.), b.p. 290-2°/0.2 mm., m.p. 178.5-179.5°. Recrystallisation of a small sample of the biscarbonate from 2-ethoxyethanol gave material of m.p. 171-3° and this was discarded. Golden (ref. 25) records m.p. 172°. It was found that the above melting points must not be carried



out with the sample in contact with soda glass, otherwise an indefinite m.p. is obtained with rapid re-solidification. The m.p. of the earlier preparation given in ref. 1 (partial melting at 160-4° followed by re-solidification) was re-determined in a Pyrex capillary and found to be 162-7°.

## 6. SULPHIDES (AND INTERMEDIATES)

### 1,3-Di(phenylthio)benzene (cf. ref. 15)

Cuprous oxide (23.8 g.), thiophenol (44 g.) and ethanol (500 ml.) were boiled under reflux in an atmosphere of nitrogen for 14 hr. The cuprous thiophenolate (54 g.) was collected by filtration, washed with ethanol and dried in vacuo.

Cuprous thiophenolate (30 g.), m-dibromobenzene (19.55 g.), quinoline (125 ml.) and pyridine (12.5 ml.) were heated to 200-210° for 5 hr. When cold the mixture was added to ice and conc. hydrochloric acid and the oil which precipitated was extracted with ether. The ether extract was washed twice with conc. hydrochloric acid and once with water and dried ( $\text{MgSO}_4$ ). The ether was evaporated and the residue was distilled to yield a red oil (21.26 g.), b.p. 187°/0.3 mm. A further distillation produced a product of similar colour (16.29 g.), b.p. 190-193°/0.8 mm. The oil was treated with acetic acid/conc. hydrochloric acid and zinc dust at 100° for 1 hr., the mixture was added to water and the product, which was now colourless, was extracted with ether. The ether extract was washed with 2N aqueous sodium hydroxide and with water and dried ( $\text{MgSO}_4$ ). The residue produced by evaporation of the ether was distilled to give 1,3-di(phenylthio)benzene as a straw coloured oil (8.7 g.), b.p. 189-190°/0.5 mm. /lit. b.p. 180-185°/0.35 mm. (ref. 23)7.

Anal. Calc. for  $\text{C}_{18}\text{H}_{14}\text{S}_2$  : C, 73.45; H, 4.8; S, 21.8

Found : C, 73.2; H, 4.8; S, 17.85%

### Pentafluorophenylsulphenyl chloride

(a) A solution of chlorine (0.0934 mole) in carbon tetrachloride (104 ml.) was added during 30 min. to a stirred solution of pentafluorothio-phenol (18.72 g., 0.0936 mole) in carbon tetrachloride (50 ml.) at -2 to -1°. The solution was stirred at 0° for 15 min. and kept at room temperature for 18 hr. Distillation of the residue remaining after evaporation of the carbon tetrachloride gave pentafluorophenylsulphenyl chloride (9.8 g.), a red oil, b.p. 36°/1.7 mm.

Calc. for  $C_6ClF_5S$  : C, 30.7; H, 0.0; Cl, 15.1; F, 40.5; S, 13.65

Found : C, 30.65; H, 0.0; Cl, 15.05; F, 40.35; S, 13.85%

A residue of low melting solid, di(pentafluorophenyl)disulphide, (7.8 g.) remained after distillation of the sulphenyl chloride.

(b) A solution of di(pentafluorophenyl)disulphide/7.8 g. residue from (a) with an additional 9.8 g. (ref. 13); total 0.088 mole  $\frac{7}{2}$  in carbon tetrachloride (100 ml.) containing chlorine (0.104 mole) was kept at room temperature for 1 hr. Distillation of the residue remaining after evaporation of the carbon tetrachloride gave pentafluorophenylsulphenyl chloride (16.5 g.), b.p. 64-66°/12 mm.

Attempted preparation of octafluoro-4,4'-di(pentafluorophenylthio)biphenyl

(a) Pentafluorophenylsulphenyl chloride (7.65 g.) in carbon disulphide (25 ml.) was added to a stirred mixture of 2,2',3,3',5,5',6,6'-octafluorobiphenyl (4.8 g.), anhydrous aluminium bromide (10.2 g.) and carbon disulphide (50 ml.). The mixture was boiled under reflux with stirring for 18 hr., kept at room temperature for 6 days, and added to dil. hydrochloric acid/ice. The carbon disulphide layer was isolated, washed with 2N hydrochloric acid and dried ( $MgSO_4$ ). Evaporation of the carbon disulphide produced a red oil, which after 20 hr. at room temperature deposited large prisms of 2,2',3,3',5,5',6,6'-octafluorobiphenyl (2.65 g.), m.p. and mixed m.p. 82-83°. A further quantity of the octafluorobiphenyl crystallised from the oil after several days at room temperature.

(b) n-Butylbromide (3.3 ml.) in ether (25 ml.) was added during 30 min. to a stirred suspension of finely divided lithium (1.18 g.) in ether (50 ml.) under nitrogen at 0-5°. The mixture was stirred at 2° for 30 min., kept at 2° for 30 min. and allowed to warm up to room temperature during 30 min. Unreacted lithium was removed by filtration under nitrogen. The ether filtrate was cooled to -60° and 2,2',3,3',5,5',6,6'-octafluorobiphenyl (3.87 g.) in tetrahydrofuran (60 ml.) was added at -60° during 45 min. with stirring under nitrogen. The mixture was stirred at -60° for 30 min. and pentafluorophenylsulphenyl chloride (6.14 g.) in tetrahydrofuran (25 ml.) was added at -60° during 45 min. with stirring under nitrogen. The mixture was stirred at -60° for 30 min., allowed to warm up to room temperature slowly and kept at room temperature for 18 hr.

2N Hydrochloric acid (25 ml.) was added and the ethers were removed by distillation. Water (100 ml.) was added to the aqueous residue and an insoluble solid was collected by filtration. The solid was extracted with boiling ethanol, insoluble material being collected by filtration of the hot mixture. Evaporation of the ethanol filtrate gave di(pentafluorophenyl) disulphide (2.1 g.), m.p. and mixed m.p. 44-51°. The solid insoluble in ethanol was extracted with boiling light petroleum (b.p. 100-120°). The petrol-insoluble material (4.1 g.), m.p. 190-198° with previous softening, did not produce a pure compound after further recrystallisation. It was shown to contain sulphur. On being cooled, the petrol filtrate gave a solid (0.42 g.), m.p. 136-140° with previous softening. This product also could not be purified further by recrystallisation. The I.R. spectrum contains no methylene absorption indicating that the product is not derived from the tetrahydrofuran solvent.

#### Attempted preparation of di(pentafluorophenyl)sulphide

Sodium nitrite (0.76 g.) was added during 1 hr. to a stirred solution of pentafluoroaniline (1.85 g.) in 70% aqueous sulphuric acid (3.6 ml.) at 0°. After having been stirred for a further 30 min. at 0° the mixture was added to a solution of pentafluorothiophenol (18 g.) in 2.25N aqueous sodium hydroxide (40 ml.) and this mixture was shaken for 10 min. The precipitated oil was extracted with ether and the ether extract was washed twice with 2N sodium hydroxide, once with water and dried (MgSO<sub>4</sub>). Evaporation of the ether produced an oil, which was distilled. The distillate (1.7 g.), b.p. 120-130°/18 mm., separated from methanol as colourless needles, m.p. 40-47°, unchanged on admixture with di(pentafluorophenyl)disulphide.

### 7. ESTERS

#### Di(pentafluorophenyl)tetrafluoroisophthalate

(a) Tetrafluoroisophthaloyl chloride (4.1 g.), prepared as under (a) (p.67) in anhydrous benzene (10 ml.) was added to pentafluorophenol (5.7 g.) in anhydrous benzene (20 ml.) and the solution was stirred at the boil whilst N,N-diethylaniline (5.8 ml.) in anhydrous benzene (10 ml.) was added over 10 min. The solution, which had turned yellow, was stirred under reflux during 2½ hr. and was allowed to stand overnight at room temperature. Crystals of the hydrochloride of N,N-diethylaniline were filtered off and the filtrates were washed successively with dil. sodium hydroxide, water, dil. hydrochloric acid, and with water until acid-free. The benzene was distilled off and the residue (7.8 g.) was recrystallised from petrol (b.p. 40-60°) to constant m.p. 91-2°. Yield 3.5 g.

Anal. Calc. for  $C_{20}F_{14}O_4$  : C, 42.1; F, 46.6; H, 0.00

Found : C, 42.3; F, 46.5; H, 0.00%

Gas chromatographic analysis (silicone gum rubber on Embacel, programmed from 100° to 300° at 15°/min., employing a flame ionisation detector) indicated a purity of ca. 95% with two or three peaks of lower retention time than the main peak.

(b) This was prepared from the acid chloride, preparation as (b) (p. 67) by reaction with pentafluorophenol in anhydrous benzene containing N,N-diethylaniline. Recrystallisation from petrol (b.p. 40-60°) yielded the ester (3.65 g.), m.p. 93-4°, purity ca. 98.5% by gas chromatography, with a component of higher retention time than the main peak.

#### 1,3-Di(pentafluorobenzoyloxy)tetrafluorobenzene

Tetrafluororesorcinol (2.73 g.) was dissolved in benzene (60 ml.) and the solution was dehydrated by azeotropic distillation, 12 ml. of benzene being removed during the procedure (the tetrafluororesorcinol may have contained water of crystallisation). Pentafluorobenzoyl chloride (6.93 g.) and N,N-diethylaniline (5.5 ml.) were added and the solution was boiled under reflux with stirring for 3 hr. After dilution with benzene (100 ml.), the solution was washed twice with 2N hydrochloric acid and once with water and was dried ( $MgSO_4$ ). The solid produced by evaporation of the benzene was recrystallised from ethanol to give the ester as colourless prisms (7 g.), m.p. 97-98°.

Anal. Calc. for  $C_{20}F_{14}O_4$  : C, 42.1; H, 0.0; F, 46.65

Found : C, 42.5; H, 0.13; F, 44.85%

#### 4,4'-Di(pentafluorobenzoyloxy)octafluorobiphenyl

The preparation of this ester has been reported previously (ref. 1) and a satisfactory analytical figure for the carbon content has now been obtained :

Anal. Calc. for  $C_{26}F_{18}O_4$  : C, 43.45; H, 0.0

Found : C, 43.45; H, 0.0.

### Di(pentafluorophenyl)tetrafluoroterephthalate

The preparation of this compound has been reported previously (ref. 1) along with unsatisfactory analytical figures from two outside laboratories. Imperial Smelting Corporation Limited have carried out the analyses reported below :

Anal. Calc. for  $C_{20}F_{14}O_4$  : C, 42.1; F, 46.6

Found : C, 42.2, 42.2; F, 46.3, 46.4

## 8. POLYESTERS

### Poly(4,4'-biphenylene isophthalate)

Isophthaloyl chloride (2.54 g.) in trichloroethylene (38 ml.) was added quickly to a rapidly stirred solution of 4,4'-dihydroxybiphenyl (2.32 g.) in water (125 ml.) containing sodium hydroxide (1.0 g.) and sodium lauryl sulphate (0.75 g.). The mixture was stirred at maximum speed for 5 min. and then added to acetone (ca. 400 ml.). The polymer (1.9 g.), m.p.  $>400^\circ$ , was collected by filtration, and the granules were crushed, washed with acetone, and water until free of chloride ion and alkali, and dried at  $100^\circ/0.2$  mm. It was insoluble in N-methylpyrrolidone, dimethylformamide, but slightly soluble in dimethylsulphoxide. See Table II for the inherent viscosity.

Calc. for  $C_{20}H_{12}O_4$  : C, 75.9; H, 3.8

Found : C, 70.9; H, 4.5

From the combustion of 4.324 mg. of polymer there was a residue of 0.109 mg.

### Poly(4,4'-biphenylene terephthalate)

Terephthaloyl chloride (5.08 g.) in trichloroethylene (75 ml.) was added quickly to a rapidly stirred solution of 4,4'-dihydroxybiphenyl (4.65 g.) in water (165 ml.) containing sodium hydroxide (2.0 g.) and sodium lauryl sulphate (1.5 g.). The polymer was worked up as described for the poly(isophthalate), above. In this case the washing with water was very slow because of the physical nature of the polymer. When free of alkali and chloride the polymer (6.2 g.) was dried at  $100^\circ/0.2$  mm. The polymer, m.p.  $>400^\circ$ , was insoluble in N-methylpyrrolidone, dimethylformamide, dimethylsulphoxide, hexamethylphosphoramide and cold conc. sulphuric acid. It was

soluble in hot conc. sulphuric acid.

Calc. for  $C_{20}H_{12}O_4$  : C, 75.9; H, 3.8

Found : C, 72.4; H, 4.2

The residue from the combustion of 4.201 mg. was 0.037 mg.

Poly(octafluoro-4,4'-biphenylene tetrafluoroisophthalate)

Tetrafluoroisophthaloyl chloride (2.75 g.) in trichloroethylene (30 ml.) was added quickly to a rapidly stirred solution of octafluoro-4,4'-dihydroxybiphenyl (3.3 g.) in water (65 ml.) containing sodium hydroxide (0.8 g.) and sodium lauryl sulphate (0.6 g.). The mixture was stirred rapidly for 5 minutes, added to acetone (200 ml.), allowed to stand overnight and filtered. The polymer (4.1 g.) collected by filtration was washed with acetone, and was washed free of alkali and chloride ion with water, and was dried in vacuo at 100°. It was soluble in dimethylformamide or N-methylpyrrolidone but was insoluble in xylene or sym-tetrachloroethane. The m.p. was over 400° but the polymer appeared to soften at ca. 300°. See Table II for the inherent viscosity.

Calc. for  $C_{20}F_{12}O_4$  : C, 45.15; H, 0.00; F, 42.8

(1) Found : C, 44.6; H, 0.11; F, 44.6

(2) Found : C, 45.3; H, 0.0; F, 42.1

Poly(octafluoro-4,4'-biphenylene tetrafluoroterephthalate)

Tetrafluoroterephthaloyl chloride (2.75 g.) and octafluoro-4,4'-dihydroxybiphenyl (3.3 g.) were converted to the polymer (4.1 g.) with the reagents, solvents, and work-up as described above. The polymer was insoluble in N-methylpyrrolidone, dimethylformamide, hexamethylphosphoramide, and conc. sulphuric acid. It did dissolve slowly in boiling dimethyl sulphoxide. The m.p. was over 400°. See Table II for inherent viscosity.

Calc. for  $C_{20}F_{12}O_4$  : C, 45.15; H, 0.00; F, 42.8

Found : C, 44.3; H, 0.15; F, 44.7

## 9. POLYAMIDES

### Poly-(m-phenyleneterephthalamide)

Terephthaloyl chloride (4.06 g.) in carbon tetrachloride (50 ml.) was added quickly to a rapidly stirred (4000 r.p.m. nominal) solution of m-phenylenediamine (distilled) (2.16 g.) in 1% aqueous sodium hydroxide (100 ml.) and stirring was continued for a further 10 min. at room temperature. The polymer (4.5 g.) was collected, washed successively and thoroughly with water, acetone and again with water, and dried at 100°/0.1 mm. for 2 hr. The polymer does not melt below 450°. See Table II for the inherent viscosity.

Calc. for  $C_{14}H_{10}N_2O_2$  : C, 70.6; H, 4.25; N, 11.75

Found : C, 65.7; H, 4.8 ; N, 10.75

### Poly(tetrafluoro-m-phenylenetetrafluoroterephthalamide)

Tetrafluoroterephthaloyl chloride (5.5 g.) in carbon tetrachloride (50 ml.) was quickly mixed with a solution of tetrafluoro-m-phenylenediamine (1.78 g.) in water (350 ml.) and immediately 5% aqueous sodium hydroxide (40 ml.) was added to the rapidly stirred mixture. Stirring was continued for a further 35 min. at room temperature. The polymer (0.85 g.) was collected, washed thoroughly with water and dried at 100°/0.1 mm. for 2 hr. The polymer does not melt below 325° at which temperature it rapidly becomes considerably darkened in air. In contrast to its hydrogen analogue, the polymer is soluble in acetone. See Table II for the inherent viscosity, and p.87 for the purity of diamine used as starting material.

Calc. for  $C_{14}H_2F_8N_2O_2$  : C, 44.0; H, 0.55; F, 39.75; N, 7.35

Found : C, 42.5; H, 1.3 ; F, 36.9 ; N, 9.2

## 10. POLYSULPHIDES

### Poly(tetrafluorophenylene sulphide)

A solution of sodium methoxide (0.05 mole) in methanol (15.5 ml.) was added to pentafluorothiophenol (10 g., 0.05 mole) and the methanol was distilled off under reduced pressure. The sodium salt was finally dried at 80°/0.1 mm. for 2 hr.

A mixture of the sodium pentafluorothiophenolate (9.25 g.), hexafluorobenzene (5.6 g.) and pyridine (85 ml.) was boiled under reflux for 1 hr. Water (1.5 l.) was added and the polymer (6.3 g.) was collected, washed successively and thoroughly with water, dil. hydrochloric acid, water, ethanol, acetone, benzene and again with acetone and dried at 100°/0.1 mm. for 2 hr. The polymer does not melt below 350° but shows signs of decomposition at this temperature in air. It is insoluble in acetone, ethanol, benzene, or dimethylformamide.

Calc. for  $C_6F_4S$  : C, 40.0; H, 0.0; F, 42.2; S, 17.8

Calc. for  $F-(C_6F_4S)_6-C_6F_5$  : C, 39.8; H, 0.0; F, 45.0; S, 15.2

Found : C, 39.85; H, 0.1; F, 44.85; S, 15.05

## 11. POLYCARBONATES

### Poly(m-phenylene carbonate)

Phosgene (ca. 6g; 0.06 mole) in tetrachloroethane (120 ml.) was added to a rapidly (ca. 1000 rpm) stirred solution of resorcinol (5.5 g; 0.05 mole) in N/1 sodium hydroxide solution (100 ml.). The emulsion remained alkaline during 3 hr. but after being stirred overnight (16 hr.) it had become acidic and 2N sodium hydroxide was added to make just alkaline. The mixture was stirred for a further 8 hr., and allowed to stand for two more days for convenience, when it was alkaline.

The white emulsion was added to acetone (400 ml.), stirred, and the coagulated polymer was collected by filtration and washed with acetone. The polymer was ground to a powder and stirred with water to extract inorganics. The polymer (4.8 g.) was collected by filtration, washed free of alkali with water and dried at 100°/0.1 mm. It was soluble in dimethyl sulphoxide, dimethyl formamide, N-methylpyrrolidone, and dimethylacetamide. The inherent viscosity, 0.12, was determined from a 0.5% solution in dimethyl sulphoxide at 30°.

Calc. for  $C_7H_4O_3$  : C, 61.7; H, 2.96

Found : C, 59.7; H, 3.44 (Residue from combustion of 4.197 mg. was 0.080 mg.)



### Poly(p-phenylene carbonate)

The preparation was carried out as described for the m-phenylene isomer using the same quantity of hydroquinone in place of resorcinol. The hydroquinone was not dissolved in the alkali until the moment before the addition of the phosgene solution. Even so, the alkaline solution turned brown, and the emulsion formed by rapid stirring of the heterogeneous mixture was coloured light brown. The polymer (5.0 g.), was obtained by adding to acetone, etc., as described for the poly(m-phenylene carbonate), was insoluble in dimethyl sulphoxide, dimethylacetamide, and hexamethylphosphoramide.

Calc. for  $C_7H_4O_3$  : C, 61.7; H, 2.96

Found : C, 57.6; H, 3.44 (Residue from combustion of  
4.425 mg. was 0.197 mg.)

### Poly(4,4'-biphenylene carbonate)

Phosgene (3 g.; 0.03 mole) in carbon tetrachloride (60 ml.) was added to a solution of 4,4'-dihydroxybiphenyl (4.65 g.; 0.025 mole) in N sodium hydroxide (150 ml.) at 20-25°, with rapid stirring (ca. 1000 rpm) over 10 min. The reaction off-white reaction mixture was stirred overnight at reduced speed, remaining alkaline over this time (ca. 20 hr.). The polymer (2.3 g.) was collected by filtration, washed with acetone, water, until free of alkali and chloride ion, and dried at 100°/0.1 mm. The inherent viscosity of this polymer could not be determined owing to its insolubility.

Anal. Calc. for  $C_{13}H_8O_3$  : C, 73.5; H, 3.8; Cl, 0.0

Found. C, 72.1; H, 4.1; Cl, 1.0

### Poly(tetrafluoro-m-phenylene carbonate)

Phosgene (3 g.; 0.03 mole) in tetrachloroethane (60 ml.) was added to a rapidly stirred and freshly prepared solution of tetrafluoro-resorcinol (4.55 g.; 0.025 mole) in N/1 sodium hydroxide solution (50 ml.). The emulsion was initially cream coloured and was found to be acidic after 2 hr., so that 2N sodium hydroxide (10 ml.) was added to make the emulsion alkaline. The addition of the further amount of alkali caused the emulsion to darken considerably and after a further 2 hr. the emulsion was again acidic. A further quantity of 2N sodium hydroxide (10 ml.) was added and the emulsion was allowed to stir overnight, when it was found to be just alkaline.

The emulsion was added to acetone (400 ml.), and the coagulated polymer suspension was stirred and collected by filtration. Both of the liquid phases in the filtrates were very dark, and the collected polymer was fawn coloured. The polymer (0.5 g.) was washed with acetone and triturated with water to free from alkali, filtered, washed with water and dried at 100°/0.1 mm.

The polymer was soluble in dimethyl sulphoxide, dimethyl acetamide, and hexamethylphosphoramide.

Calc. for  $C_{74}F_{40}O_3$  : C, 40.4; H, 0.00; F, 36.5

Found : C, 37.8; H, 0.19; F, 33.7

Inherent viscosity : 0.026, determined from 0.5% solution in dimethyl sulphoxide at 30°.

#### Attempted preparation of poly(tetrafluoro-p-phenylene carbonate)

With tetrafluorohydroquinone (3 g.) in place of tetrafluoro-resorcinol the preparation was carried out as described for the isomeric tetrafluoro-m-phenylene polymer. Much more 2N sodium hydroxide (30 ml.) had to be added to maintain the emulsion alkaline, and on work up as described for the isomeric polymer a negligible yield was obtained - very dark coloured liquor was obtained on adding the dark emulsion to acetone.

#### Poly(octafluoro-4,4'-biphenylene carbonate)

(a) Phosgene (2 g.; 0.02 mole) in sym.-tetrachloroethane (60 ml.), was added to a rapidly stirred solution of octafluoro-4,4'-dihydroxybiphenyl (5.5 g.; 0.0167 mole), in N/1 sodium hydroxide (50 ml.) at 5-7° over 10 min. There was an exothermic reaction, and the emulsion was allowed to stir for 19 hr. at room temperature after the addition. The polymer was collected by filtration, washed with acetone and water until free of alkali. The polymer (2.65 g.) was dried at 100°/0.1 mm. for 5 hr., during which time a trace of sublimate was formed. The polymer dissolved readily in hot dimethyl sulphoxide, dimethylacetamide, or hexamethylphosphoramide.

Anal. Calc. for  $C_{138}F_{80}O_3$  : C, 43.8; H, 0.00; Cl, 0.00; F, 42.7

Found : C, 44.3; H, 0.48; Cl, 0.00; F, 35.05

Inherent viscosity : 0.02 dl./g., determined from a 0.5% solution in dimethyl sulphoxide.

(b) Via octafluoro-4,4'-bis(chloroformyloxy)biphenyl.

Octafluoro-4,4'-dihydroxybiphenyl (6.6 g., 0.02 mole) in anhydrous ether (20 ml.) was added to a solution of phosgene (12 g., 0.121 mole) in anhydrous ether (50 ml.) at  $-3^{\circ}$ , rising to  $4^{\circ}$  during the addition. Over 12 min. at below  $5^{\circ}$  a solution of N,N'-diethylaniline (6.6 ml., 0.041 mole) in anhydrous ether (20 ml.) was added. The mixture was allowed to stir, rising to room temperature, overnight (total time : 24 hr.), and was allowed to stand for a further period overnight. The hydrochloride of diethylaniline was separated by filtration and the residual phosgene and the ether were distilled off, finally in vacuo, from the steam bath. A gum was obtained that could not be recrystallised or solidified.

In order to obtain more of this product for purification by distillation the experiment was carried out again on twice the above scale, and it was attempted to distil the combined products. Only a trace of distillate came over, at ca.  $100^{\circ}/18$  mm., which solidified in the air condenser. Thereafter the pressure in the system rose to 100 mm. due to decomposition, and on cooling the contents of the still became very viscous, still giving off bubbles of gas.

By heating the still contents further it was hoped to obtain a polycarbonate. Solidification occurred on gentle heating to  $100^{\circ}$  (bath) and only softening occurred on raising the temperature to  $200^{\circ}$  (bath). The product was kept at  $200^{\circ}$  for 1 hr., and allowed to cool in the desiccator. The mauve product (ca. 18 g.) smelled of phosgene and was brittle when cold. It was insoluble in dimethyl sulphoxide, but dissolved in hot hexamethylphosphoramide or hot dimethylacetamide, but not in the cold. A small amount of effervescence was noted in these hot solvents as the product dissolved. This may have been due to the reaction of residual chloroformoxy groups with impurities, e.g. moisture in the solvents, or due to phosgene trapped in the solid. There was only a trace of chlorine, and a trace of hydrogen was found when the product was analysed. The low fluorine figure is probably a suspect determination.

Anal. Calc. for  $C_{13}F_8O_3$  : C, 43.8; H, 0.00; Cl, 0.00; F, 42.7

Found : C, 44.7; H, 0.22; Cl, 0.2 ; F, 35.6

## 12. POLYIMIDES

### Polypyromellitimides

Six polypyromellitimides have been prepared from pyromellitic anhydride and six aromatic diamines (m- and p-phenylene diamine, benzidine, and the three fluoro-analogues). Each polymer was prepared by the same general method:

The polyamic acid was prepared first by slowly adding pyromellitic dianhydride (1 mol.) to a stirred solution of the diamine (1 mol.) in N,N-dimethylacetamide (sufficient to produce a 10% w/v solution of polyamic acid) at room temperature. The N,N-dimethylacetamide was estimated to contain not more than 2% of water, from the infra-red spectrum.

Stirring was continued for 45 min. at room temperature and afterwards at 50° for 45 min. The solution of polyamic acid was evaporated to dryness on a hot plate and the solid film produced was heated at 300° for 15 min. To ensure complete cyclisation to polypyromellitimide, the polymer was heated at 300°/0.15 mm. for 1.5 hr.

The inherent viscosities of two of these polymers were determined at the soluble stage, i.e. at the polyamic acid stage. Samples of the solution were diluted with N,N-dimethylacetamide.

Poly(m-phenylenepyromellitimide) from m-phenylenediamine and pyromellitic dianhydride

Calc. for  $C_{16}H_6N_2O_4$  : C, 66.2; H, 2.1; N, 9.65

Found : C, 63.85; H, 2.35; N, 8.9

Poly(p-phenylenepyromellitimide) (XXX) from p-phenylenediamine and pyromellitic dianhydride

Calc. for  $C_{16}H_6N_2O_4$  : C, 66.2; H, 2.1; N, 9.65

Found : C, 63.65; H, 2.55; N, 9.5

Poly(4,4'-biphenylylenepyromellitimide) from benzidine and pyromellitic dianhydride

Calc. for  $C_{22}H_{10}N_2O_4$  : C, 72.15; H, 2.75; N, 7.65

Found : C, 69.95; H, 3.4; N, 8.05

Inherent viscosity of intermediate polyamic acid : 0.47 dl./g., determined using a 1% (w/v) solution in N,N-dimethylacetamide at 30°C.

Poly/(tetrafluoro-m-phenylene)pyromellitimide / from tetrafluoro-m-phenylene-diamine and pyromellitic dianhydride . See page 87 for the purity of the diamine.

Calc. for  $C_{16}H_2F_4N_2O_4$  : C, 53.05; H, 0.55; F, 21.0; N, 7.75

Found : C, 52.65; H, 1.2 ; F, 21.1; N, 7.85

Poly/(tetrafluoro-p-phenylene)pyromellitimide / (XXXI) from tetrafluoro-p-phenylenediamine and pyromellitic dianhydride

Calc. for  $C_{16}H_2F_4N_2O_4$  : C, 63.05; H, 0.55; F, 21.0; N, 7.75

Found : C, 51.05; H, 1.25; F, 21.45; N, 8.1

Poly/(octafluoro-4,4'-biphenylene)pyromellitimide / from 4,4'-diamino-octafluorobiphenyl and pyromellitic dianhydride

Calc. for  $C_{22}H_2F_8N_2O_4$  : C, 51.75; H, 0.4; F, 29.8; N, 5.5

Found : C, 51.2; H, 0.95; F, 29.4; N, 5.6

Inherent viscosity of intermediate polyamic acid: ca. 0.06 dl./g., determined using a 0.5% (w/v) solution in N,N-dimethylacetamide at 30°C.

Intermediate polyamic acid for poly(m-phenylenepyromellitimide)

A solution of m-phenylenediamine (freshly distilled) (5.407 g., 50.00 mM.) in N-methyl-2-pyrrolidone (dried over CaO, distilled and dried over molecular sieve; containing ca. 1% of lower boiling impurity (possibly a trace of NH absorption was observed in the infra-red spectrum of the solvent) (160 ml.) was stirred at room temperature (20-25°) whilst pyromellitic dianhydride was added in carefully controlled amounts. Stirring was continued at room temperature for ca. 30 min. after each addition, and the inherent viscosity of the polyamic acid was determined; occasionally the solution was stirred for a much longer period after an addition, to observe any change in viscosity with time. The inherent viscosity, which was determined at 30.1°C. on a 0.5% (w/v) solution in N-methyl-2-pyrrolidone using a No. 100 viscometer tube, reached a maximum when 50.2 mM. of pyromellitic dianhydride had been added. Subsequent additions gave small decreases in viscosity. The viscosity results are indicated in the table over :

Total accumulated wt. of pyromellitic dianhydride	Time of stirring of polymer soln. at room temp. after addition	Inherent viscosity (dl./g.)
10.506 g. (48.19 mM)	-	-
10.716 g. (49.15 mM)	30 min.	0.438
10.831 g. (49.65 mM)	30 min.	0.641
10.946 g. (50.21 mM)	30 min.	0.833
	18 hr.	0.857
11.056 g. (50.7 mM)	30 min.	0.848
	3 hr.	0.850
11.160 g. (51.16 mM)	30 min.	0.839
	18 hr.	0.828

### 13. POLYHYDRAZIDES

The dimethylacetamide and N-methylpyrrolidone used in the following polymer preparations contained small amounts of water despite drying over calcium oxide followed by fractionation. The quantities of water were estimated from infra-red spectra and were  $\frac{1}{2}$ % and  $\frac{1}{4}$ % respectively.

#### Poly(terephthalhydrazide)

Terephthaloyl chloride (4.06 g.; 0.02 mole) was dissolved in dimethylacetamide (25 ml.) by warming and the solution was cooled to below 15°, with stirring. Anhydrous hydrazine (0.6 ml.; 0.019 mole) in dimethylacetamide (25 ml.) was added over 15 min. keeping the temperature below 15°. An exothermic reaction was observed. The mixture was allowed to stir overnight at room temperature, and added to water (500 ml.). The aqueous suspension of polymer was stirred 5 min. and filtered. The collected polymer (3.1 g.) was washed free of acid and dried at 100°/0.1 mm. for 2 hr.

This polymer was insoluble in dimethylformamide, N-methylpyrrolidone, dimethylacetamide, dimethyl sulfoxide and hexamethylphosphoramide. It may contain adsorbed water, although the analysis is not very satisfactory:

Calc. for  $C_8H_6N_2O_2$  : C, 59.2; H, 3.73; N, 17.32

Calc. for  $C_8H_8N_2O_3$  : C, 53.3; H, 4.48; N, 15.56

Found : C, 55.2; H, 3.84; N, 15.1.

### Poly(isophthalhydrazide)

(a) Preparation in dimethylacetamide. - Anhydrous hydrazine (1.28 ml.; 0.04 mole) in dimethylacetamide (50 ml.) was added to a stirred solution of isophthaloyl chloride (8.12 g.; 0.04 mole) in dimethylacetamide (50 ml.) over 15 min. at 10-15°. The solution was stirred for a further 45 min. at 10-15° and allowed to stir at room temperature for 16 hr. The polymer (6.3 g.), precipitated by adding the solution to water (500 ml.), was collected by filtration, washed free of acid, and dried at 100°/0.1 mm. to constant weight. When dried initially at 56°/0.1 mm. this polymer still retained a considerable amount of moisture. Even after being dried at 100°/0.1 mm. the elemental analysis indicates the presence of water (approx. a monohydrate of the polymer unit) and this appeared to be confirmed by weight loss during heating the polymer to ca. 290° on the thermobalance. Further weight loss occurred only at ca. 290° and above: this second weight loss is presumably due to cyclisation to the poly(oxadiazole). As shown by the infra-red spectrum, such cyclisation seemed to occur when the polyhydrazide was heated at 0.1 mm. for 30 min. at 280°.

Calc. for  $C_8H_6N_2O_2$  : C, 59.2; H, 3.73; N, 17.3

Calc. for  $C_8H_8N_2O_3$  : C, 53.3; H, 4.48; N, 15.56

Found : C, 52.7; H, 4.69; N, 16.7

Inherent viscosity : 0.16 dl./g., determined from 0.5% solution in dimethyl sulphoxide at 30°. Also found : 0.14 dl./g., from 0.5% solution in dimethylacetamide. Frazer and Wallenberger (ref. 18) record an inherent viscosity 1.0 dl./g. in dimethyl sulphoxide.

(b) Preparation in N-methylpyrrolidone. The preparation was carried out as described under (a) above but using N-methylpyrrolidone in place of dimethylacetamide. The polymer (6.4 g.) was dried at 100°/0.1 mm.

Inherent viscosity : 0.19 dl./g., determined from 0.5% solution in dimethyl sulphoxide at 30°.

(c) Preparation in N-methylpyrrolidone/lithium chloride. - Lithium chloride was dehydrated at 100°/0.1 mm. and used to form a 5% (weight/volume) solution in N-methylpyrrolidone. On addition of hydrazine (1.28 ml.) to this solution (50 ml.) there was precipitation of lithium chloride, which required a further amount of solvent (10 ml.) to redissolve it. This solution was added to a solution of isophthaloyl chloride (8.12 g.), stirred at 10-15°, over 15 min. The solution was stirred at this temperature for a further 1 hr. and allowed to stir overnight at room temperature. The polymer was precipitated by adding the solution to water (300 ml.), the temperature of the mixture rising to 32°. Cooling whilst stirring brought the temperature to 20° in a few minutes and the mixture was filtered. The white polymer (6.15 g.) was dried at 100°/0.1 mm.

Inherent viscosity : 0.21 dl./g., determined from 0.5% solution in dimethyl sulphoxide at 30°.

Poly(tetrafluoroterephthalhydrazide)

(a) Preparation from Hydrazine and Tetrafluoroterephthaloyl Chloride in Dimethylacetamide. - Hydrazine (0.64 ml.; 0.02 mole) in dimethylacetamide (25 ml.) was added to a stirred solution of tetrafluoroterephthaloyl chloride (5.5 g.; 0.02 mole) in dimethylacetamide (25 ml.), at 10-15°, during 15 min. The mixture was stirred overnight, the polymer separating from solution. Water (100 ml.) was added, and the polymer (4.4 g.) was collected by filtration, washed free of acid with water, and dried at 100°/0.1 mm. The polymer dissolves in dimethyl formamide, N-methylpyrrolidone, dimethylacetamide, dimethyl sulphoxide, and hexamethylphosphoramide.

Calc. for  $C_8H_2F_4N_2O_2$ : C, 41.0; H, 0.88; F, 32.5; N, 12.0

Found : C, 41.9; H, 1.74; F, 37.7; N, 10.4

Inherent viscosity : 0.16, determined from 0.5% solution, in dimethylacetamide at 30°, from which a trace of insolubles had been removed by filtration.

(b) Preparation from Hydrazine and Tetrafluoroterephthaloyl chloride in N-methylpyrrolidone/lithium chloride. - A solution of anhydrous lithium chloride (1.25 g.) and hydrazine (0.64 ml.; 0.02 mole) in N-methylpyrrolidone (30 ml.) was added to a solution of tetrafluoroterephthaloyl chloride (5.5 g.; 0.02 mole) with the formation of a golden brown solution. The addition was carried out at 10-15° over 15 min. The solution was stirred at 10-15° for 1 hr., then at room temperature overnight, and was added to water (150 ml.). An off-white precipitate of polymer was formed and the temperature of the



suspension rose to 35°. The mixture was stirred with external cooling, to room temperature and the polymer (4.3 g.) collected by filtration, washed free of acid and dried at 100°/0.1 mm.

Inherent viscosity : 0.11 dl./g., determined from 0.5% solution in dimethyl sulphoxide at 30°.

(c) Preparation from tetrafluoroterephthaldihydrazide and terephthaloyl chloride in dimethylacetamide. - Tetrafluoroterephthaloyl chloride (2.75 g.; 0.01 mole) in dimethylacetamide (10 ml.) was added to a stirred solution of tetrafluoroterephthaldihydrazide (2.66 g.; 0.01 mole) in dimethylacetamide (40 ml.) at 10-15°, with occasional cooling, during 15 min. Polyhydrazide separated from the solution while being stirred overnight at room temperature. The mixture was added to water (200 ml.), the polymer was collected by filtration, washed free of acid with water, and dried at 100°/0.1 mm.

Inherent viscosity : 0.16 dl./g., determined from 0.5% solution in dimethylacetamide (cloudy solution from which a trace amount of insoluble matter had been removed by filtration), at 30°.

#### Poly(tetrafluoroisophthalhydrazide)

Tetrafluoroisophthaloyl chloride (5.5 g.; 0.02 mole) was converted to the polyhydrazide (4.6 g.) in dimethylacetamide as described for the isomeric poly(tetrafluoro-p-phenylene hydrazide) by method (a).

Inherent viscosity : 0.086 dl./g., determined from 0.5% solution in dimethylacetamide.

Calc. for  $C_8H_2F_4N_2O_2$  : C, 41.02; H, 0.86; F, 32.46; N, 13.66

Calc. for  $C_8H_4F_4N_2O_3$  : C, 38.6; H, 1.59; F, 30.15; N, 11.12

Found : C, 44.1; H, 1.9; F, 30.05; N, 10.9

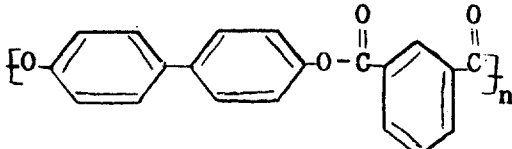
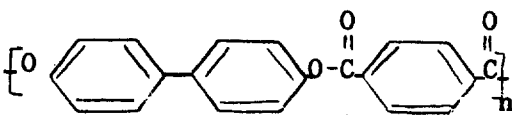
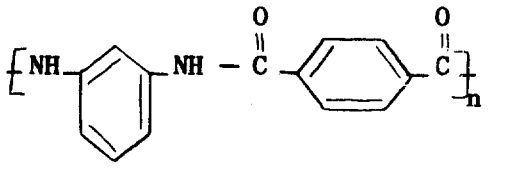
#### 14. STABILITY OF POLYMERS HEATED IN AIR

(a) In preliminary experiments to obtain a comparison of the effect of heating the polymers in air, a small sample (50 mg.) of the polymer was placed in a small pyrex tube (3 cm. length, 4 mm. internal diameter), open at the upper end, and this container was placed in a larger tube (35 cm. length, 6 mm. internal diameter) also open to air at the upper end. The lower end of the larger tube was inserted in a salt bath heated at 300°C,

and the loss in wt. of the polymer was determined after a suitable time interval at this temperature. The results, which are shown in Table II, indicate that each fluoro-polymer is less stable than its hydrogenic analogue. The infra-red spectra of sublimates formed from the perfluorinated polyesters were examined, but although CO and OH absorption was observed, the sublimates were not characterised.

The inherent viscosities of the polymers are also given in Table II. This emphasises that the polymers probably have low molecular weights, which may lower their thermal stabilities. The inherent viscosities of the polyesters were determined in 0.5% solutions in dimethyl sulphoxide; those of the amides were determined in 0.5% solutions in 98% sulphuric acid.

**TABLE II**

Polymer Skeletal Structure	Duration of heating at 300°C	% Loss in wt.		Inherent Viscosity at 30°C	
		H-polymer	F-polymer	H-polymer	F-polymer
	21.5 hr.	4.2%	20.6%	0.11 (0.25% solution)	0.03
	21.5 hr.	6.7%	12.9%	(insol.)	0.02
	2.0 hr.	1.1%*	20.0%	0.41	0.04

\* Dine-Hart, Moore, and Wright (ref. 26) have reported a weight loss of 1.8% for this polymer after 2 hr. at 300°C in air.

(b) The polyimides (XXX) and (XXXI) placed in an alumina crucible were heated in air in the furnace of a Stanton HTD Thermogravimetric Balance, with the weight losses as shown below. The temperatures are probably correct to  $\pm 5^\circ$ . The rate of rise between the steady temperatures was  $6^\circ\text{C min}^{-1}$ .

Hydrogenic Polyimide (XXX)

Sample weight .... 81.2mg.

At 397°C for 24 hr.

Average weight loss over 24 hr.  
0.18%/hr.

Final weight loss 0.03%/hr.

At 450°C for 26 hr.

Fairly constant weight loss over  
26 hr. 1.0%/hr.

Perfluorinated Polyimide (XXXI)

Sample weight .... 84.5mg.

At 312°C for 21 hr.

Average weight loss over 21 hr.  
0.18%/hr.

Final weight loss over 10 hr. 0.49%/hr.

At 332°C for 102.5 hr.

Average weight loss over 102.5 hr.  
0.21%/hr.

Final weight loss over 33.5 hr.  
0.094%/hr.

At 352°C for 50 min.

Average weight loss over 50 min.  
0.39%/hr.

At 402°C for 50 min.

Average weight loss over 50 min.  
2.8%/hr.

(c) A sample of the polycarbonate of inherent viscosity 0.02, derived from octafluoro-4,4'-dihydroxybiphenyl was heated in a platinum crucible in air at  $220^\circ$  for 5 hr., with a weight loss of 5.5%. When the temperature was raised to  $330^\circ$ , and the sample kept at this temperature for 5 hr., there was a further weight loss. The total weight loss was 40.5%. This is probably a polymer of low molecular weight (preparation : Section C, 11).

E. FUTURE PLANS (arising from the work reported)

1. The synthesis of imide, benzoxazole, benzthiazole, and benzimidazole, perfluorinated model compounds, which on the basis of work already done may have high thermal decomposition temperatures.

2. The preparation of polymers of high inherent viscosity, and if possible of known molecular weight range, for determination of thermal and oxidative stability in both the perfluorinated and hydrogenic series. Such polymers should include polyimides, polyhydrazides, polyoxadiazoles, polycarbonates, polyesters, and other polymers that seem likely to have stabilities at least equal to those of the hydrogenic polymers. These polymer types are chosen on the basis of the thermal decomposition temperatures of the model compounds. A thermobalance will be employed for weight loss determinations at elevated temperatures.

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## APPENDIX A

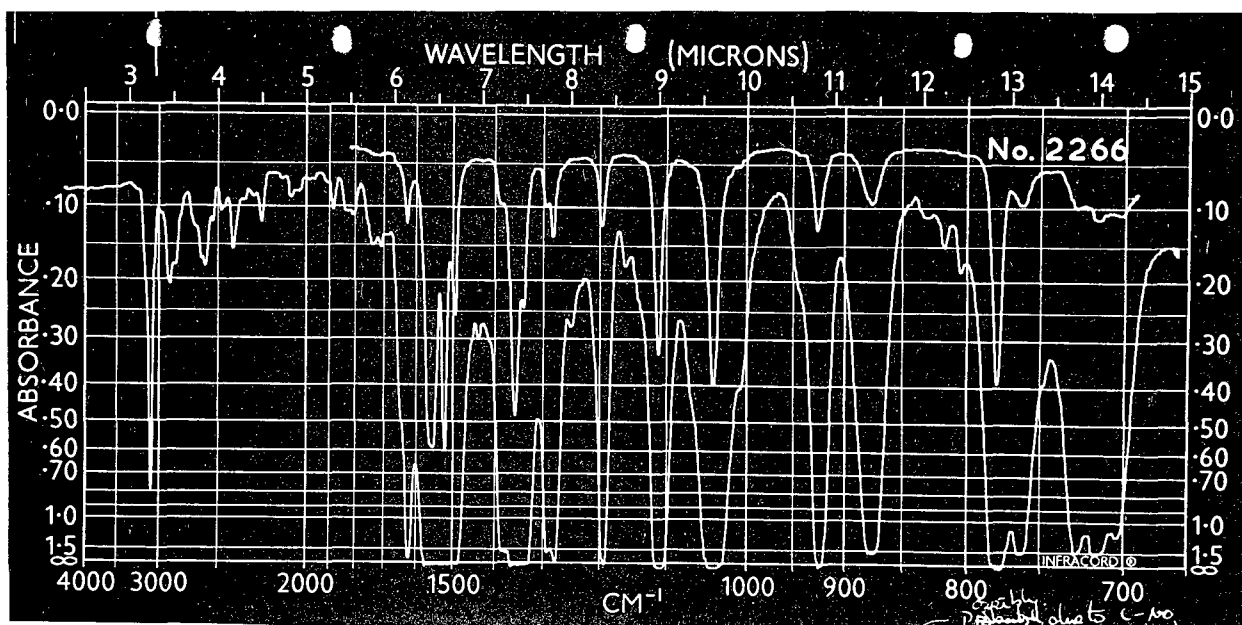
### Infra-red Spectra Referred to in Part I

<u>No.</u>	
2266	2,3,4,5-Tetrafluoronitrobenzene (film)
2453	2,3,4,5-Tetrafluoroaniline (film)
2741	2-Nitro-3,4,5,6-tetrafluoroaniline (film)
2745	4,4'-Dinitro-octafluorobiphenyl (in CCl <sub>4</sub> )
2815	Tetrafluoroisophthalic acid (KBr disc)
2901	Tetrafluoro-o-phenylenediamine (in CCl <sub>4</sub> )
2907	3,3'-Diamino-4,4'-dinitrohexafluorobiphenyl (in CCl <sub>3</sub> CN)
2917	4-Aminotetrafluorobenzonitrile (KBr disc)
3040	3,4,3',4'-Tetraminohexafluorobiphenyl (KBr disc)
3075	Tetrafluororesorcinol (KBr disc)
3076	Tetrafluororesorcinol (in CCl <sub>3</sub> CN)
3137	Tetramethyl dichloropyromellitate (in CCl <sub>4</sub> )
3138	Tetrafluoro-p-phenylenediamine (in CCl <sub>4</sub> )
3208	Decafluorodiphenylamine (KBr disc)
3209	Impure difluoropyromellitic acid from acid hydrolysis of suspected p-difluorotetracyanobenzene (KBr disc)
3210	Dichloropyromellitoylchloride (Nujol and hexachlorobutadiene mulls)
3247	1,3-Bis(pentafluorophenylthio)tetrafluorobenzene (KBr disc)
3264	6,6'-Bis(2,3-diphenyl-5,7,8-trifluoroquinoxalyl) (KBr disc)

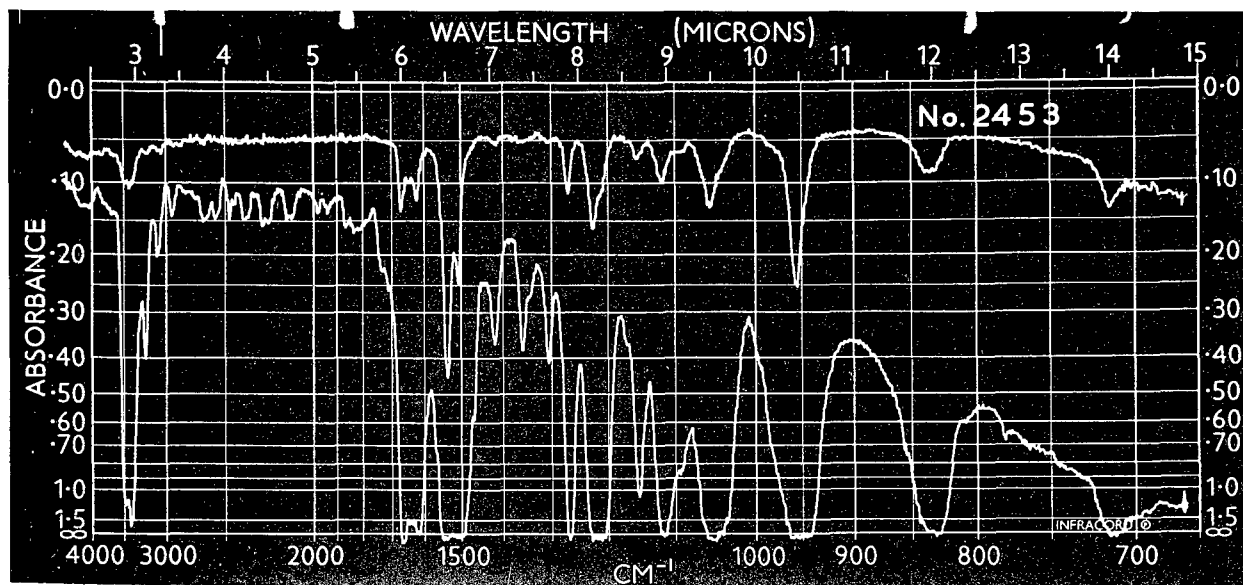
APPENDIX A (CONT'D)

<u>No.</u>	
3265	1,4-Bis(pentafluorophenylthio)tetrafluorobenzene (KBr disc)
3266	1,4-Bis(pentafluoroanilino)tetrafluorobenzene (in CCl <sub>3</sub> CN)
3269	4,4'-Bis(pentafluorophenylthio)octafluorobiphenyl (KBr disc)
3271	3,3'-Dihydroxy-4,4'-dinitrohexafluorobiphenyl (in CCl <sub>3</sub> CN)
3282	Tetramethyl difluoropyromellitate (KBr disc)
3283	4-Fluorodurenediazonium borofluoride (film)
3284	Difluorodurene (in CCl <sub>4</sub> )
3292	1,4-Bis(methylthio)tetrafluorobenzene (in CCl <sub>4</sub> )
3334	3,3'-Dihydroxy-4,4'-diaminohexafluorobiphenyl (in CCl <sub>3</sub> CN)
3351	Difluoropyromellitic acid (KBr disc)
3353	Pentabromobenzotrifluoride (KBr disc)
3362	Impure difluoropyromellitic acid after treatment with nitrous acid (KBr disc)
3376	Tetramethyl difluoropyromellitate (in CCl <sub>4</sub> )
3376a	Tetramethyl difluoropyromellitate (KBr disc)
3389	Impure 3-bromoheptafluorotoluene (film)
3390	2,3,4,6-Tetrafluoroacetanilide (in CHCl <sub>3</sub> )
3397	Octafluoronaphthalene (in CCl <sub>4</sub> )
3782	2,3,4,6-Tetrafluoroaniline (film)
3784	3,4,3',4'-Tetra(trifluoroacetimido)hexafluorobiphenyl (Kel F, hexachlorobutadiene and Nujol mulls)

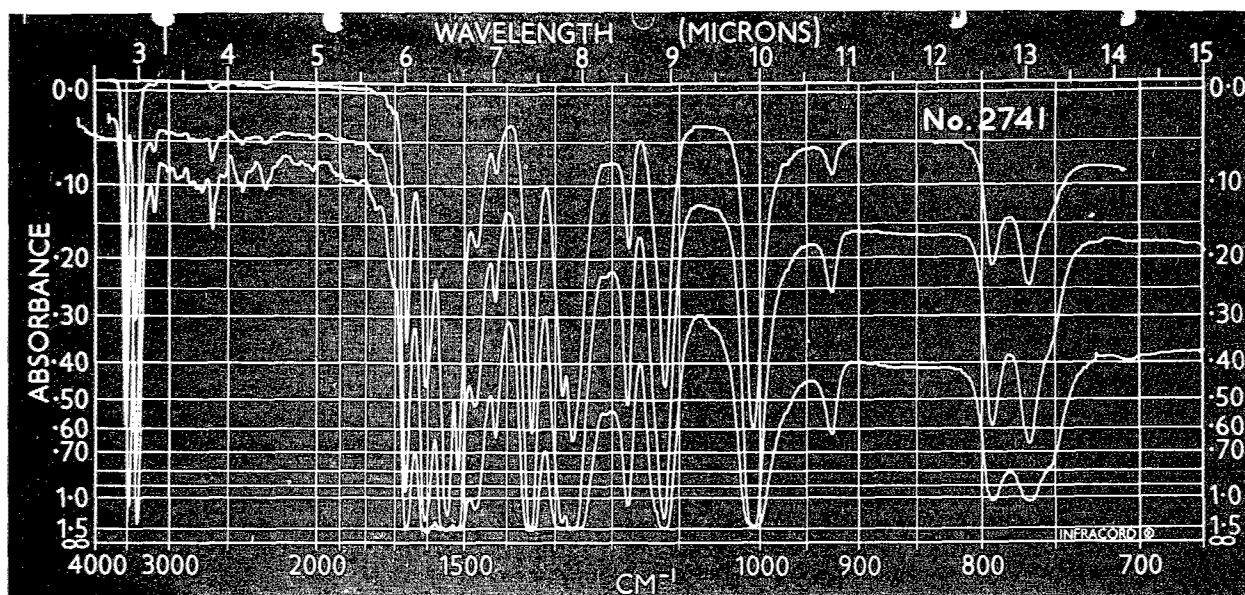




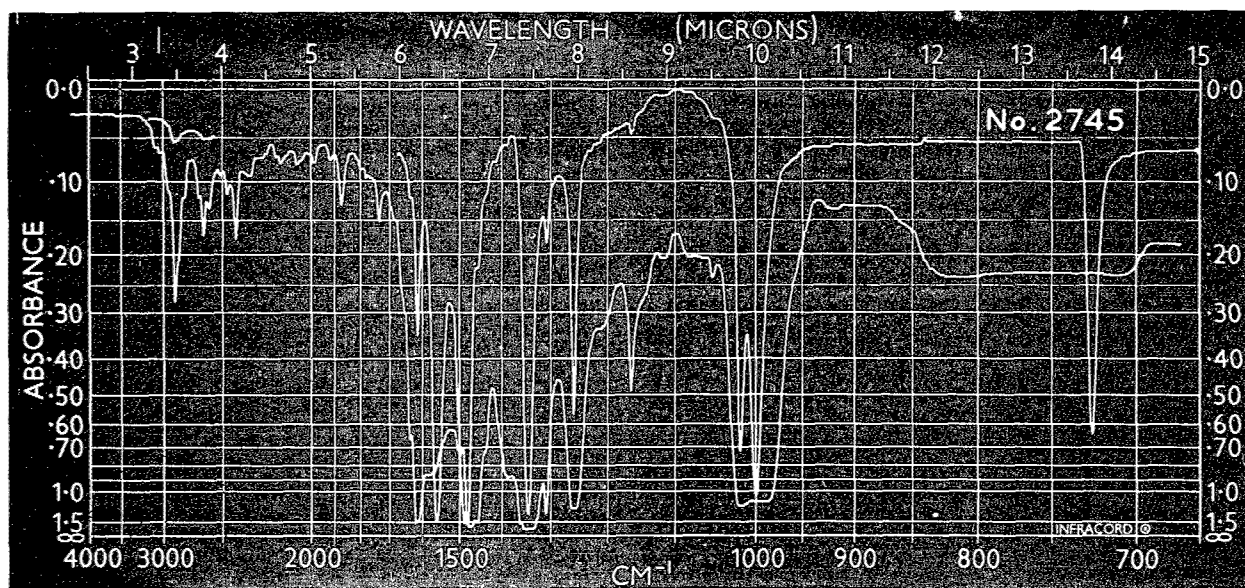
Spectrum No. 2266      2,3,4,5-Tetrafluoronitrobenzene (film)



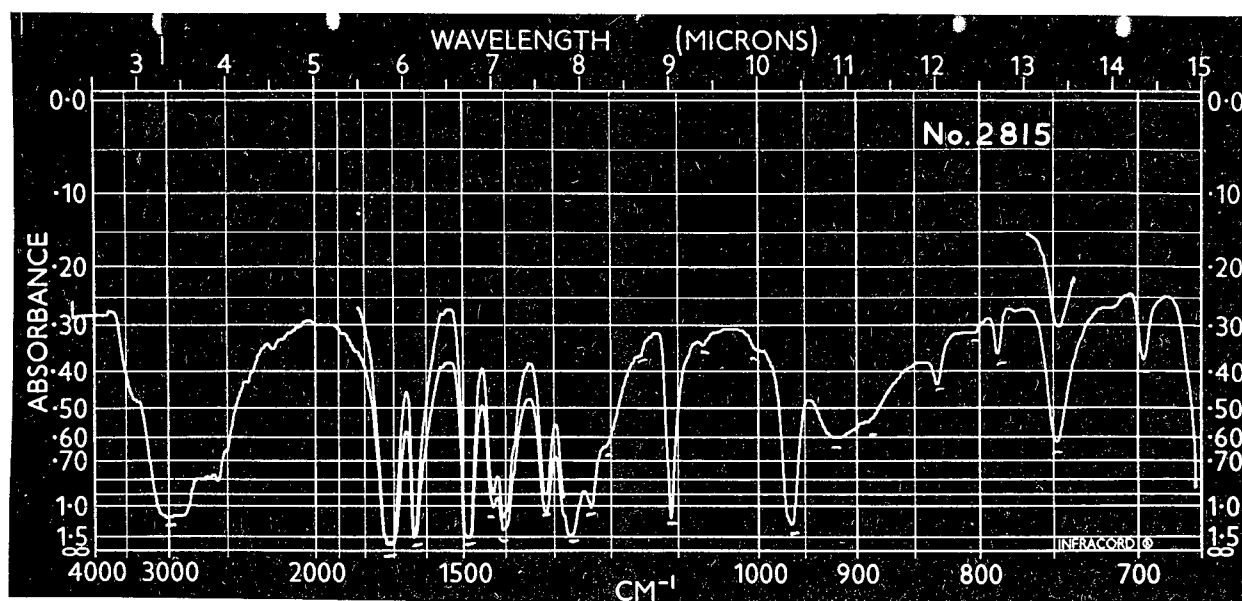
Spectrum No. 2453      2,3,4,5-Tetrafluoroaniline (film)



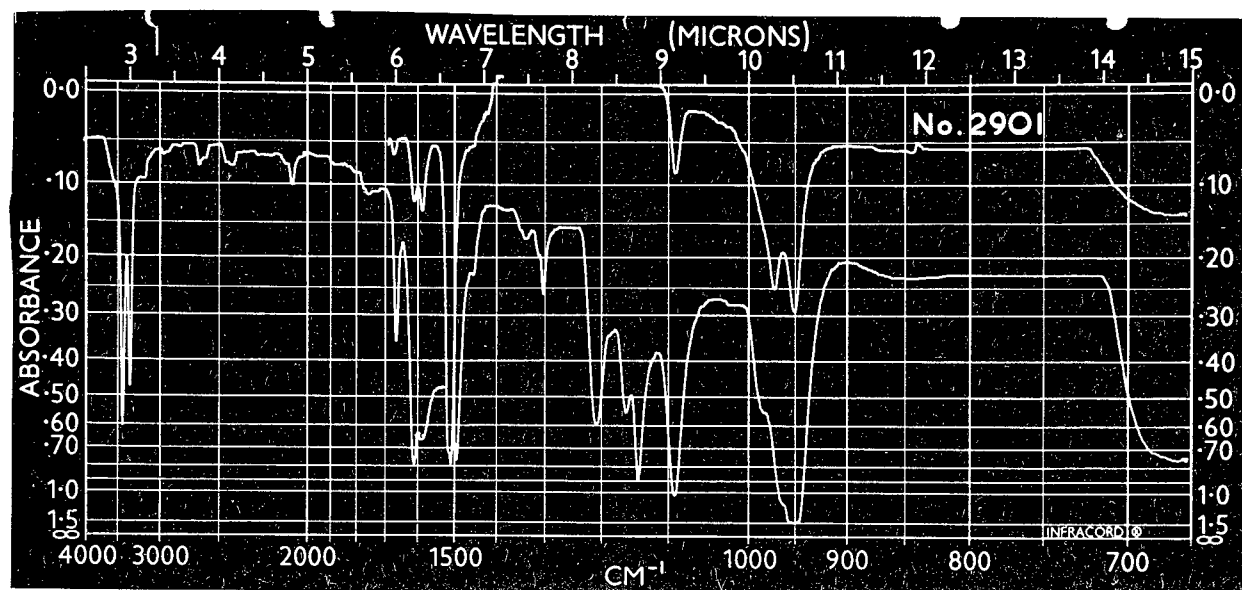
Spectrum No. 2741      2-Nitro-3,4,5,6-tetrafluoroaniline (film)



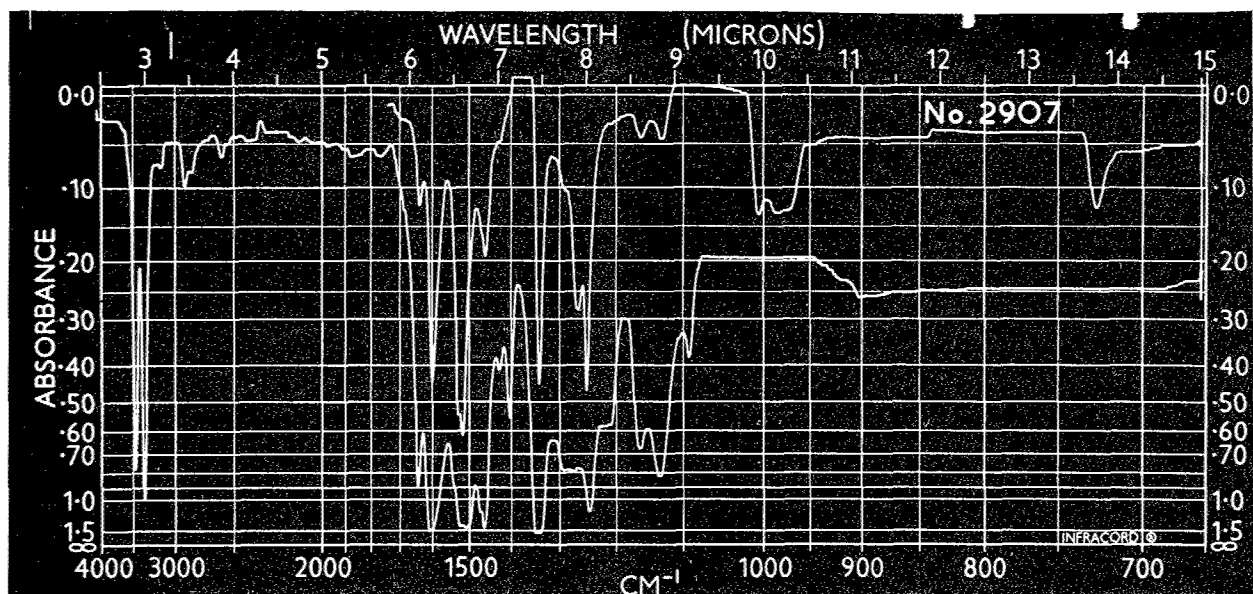
Spectrum No. 2745      4,4'-Dinitro-octafluorobiphenyl (in CCl<sub>4</sub>)



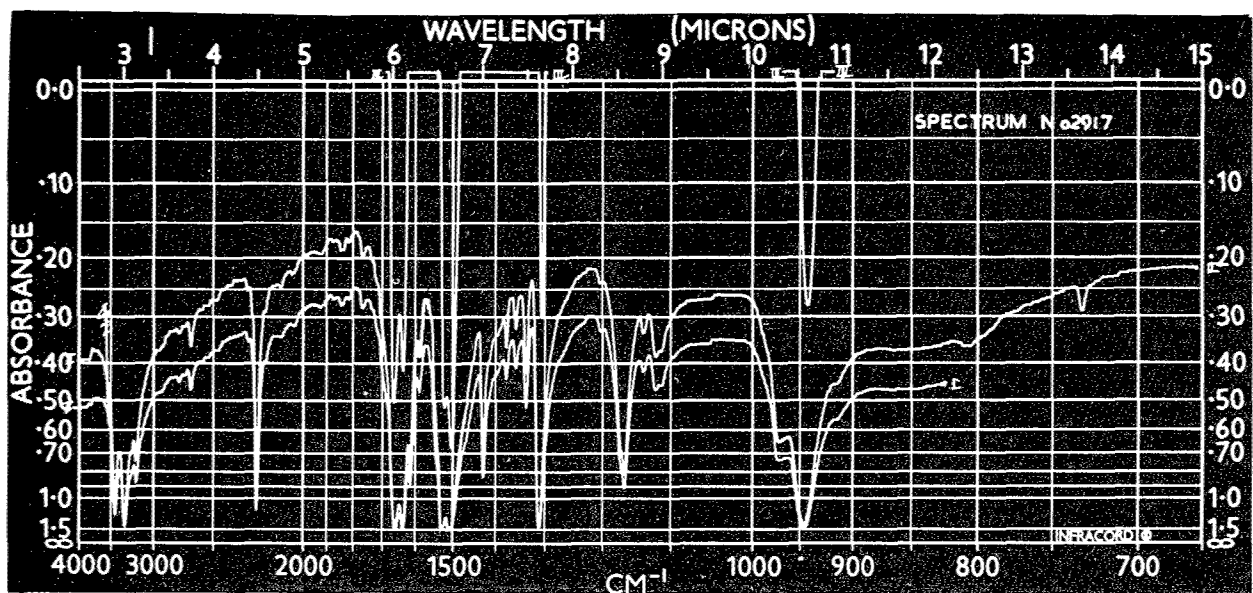
Spectrum No. 2815      Tetrafluoroisophthalic acid (KBr disc)



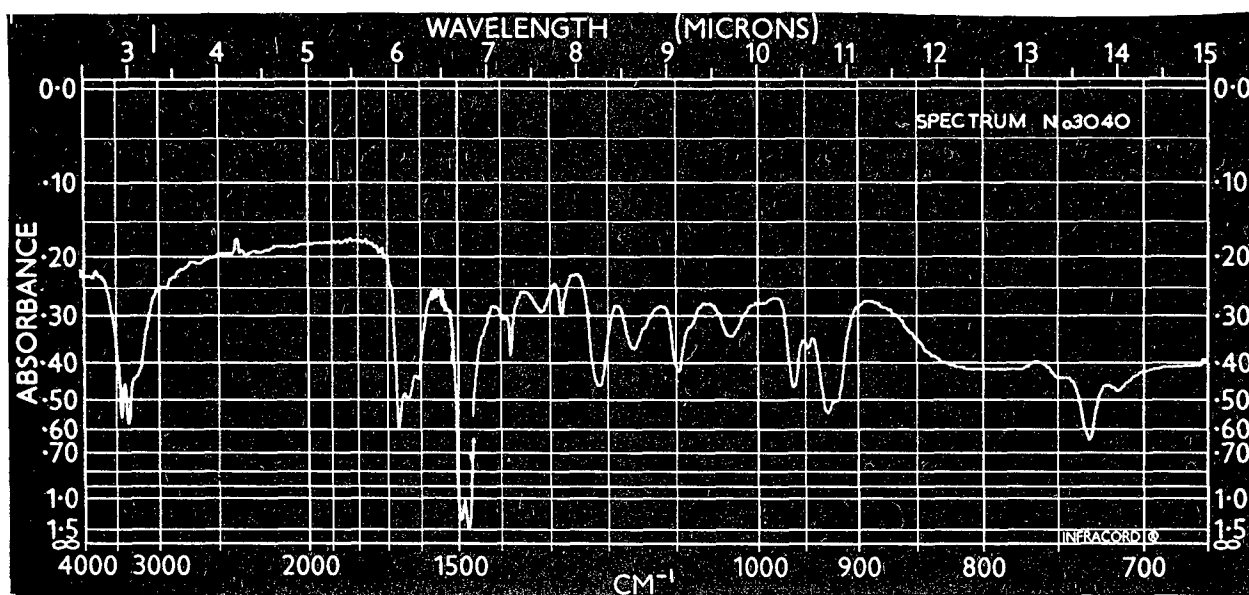
Spectrum No. 2901      Tetrafluoro-o-phenylenediamine (in CCl<sub>4</sub>)



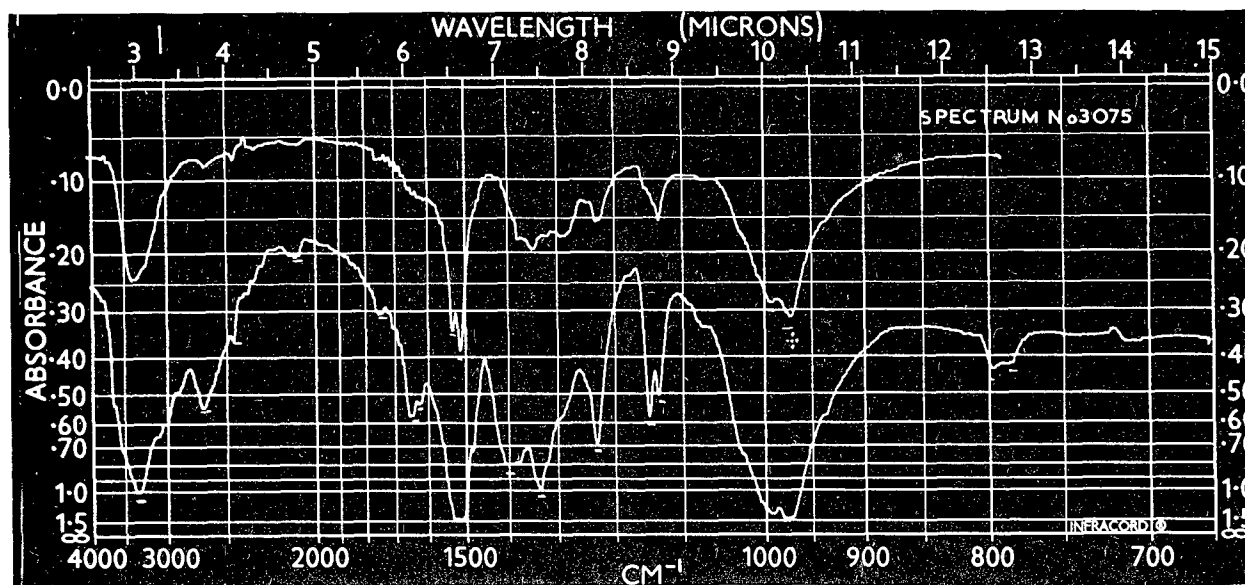
Spectrum No. 2907      3,3'-Diamino-4,4'-dinitrohexafluorobiphenyl  
(in  $\text{CCl}_3\text{CN}$ )



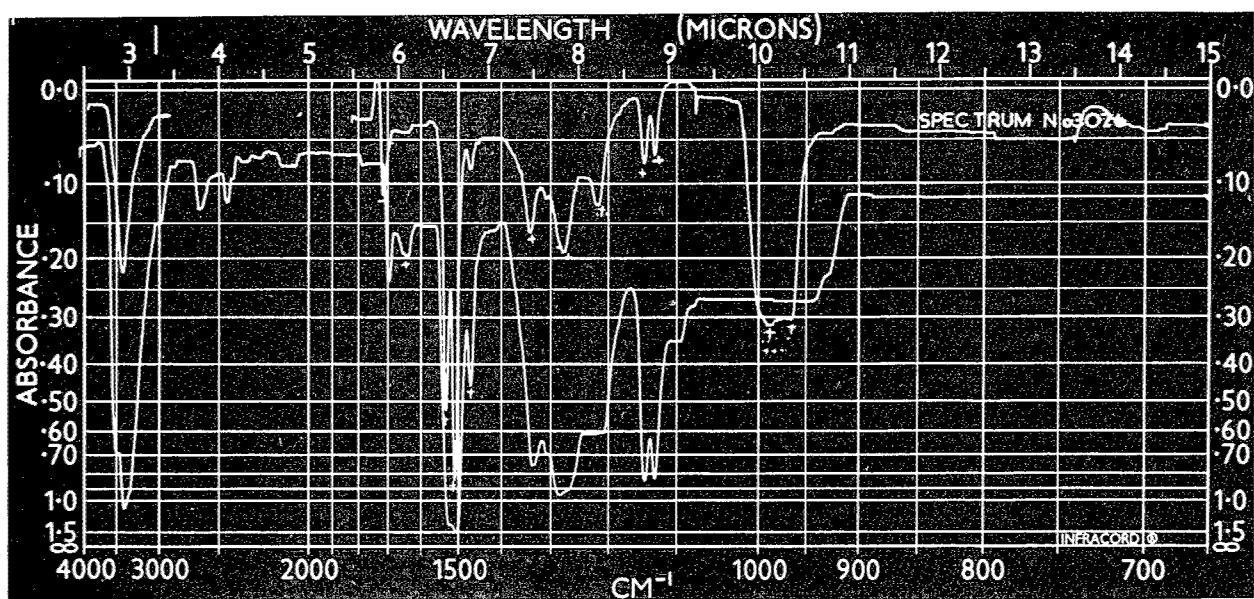
Spectrum No. 2917      4-Aminotetrafluorobenzonitrile (KBr disc)



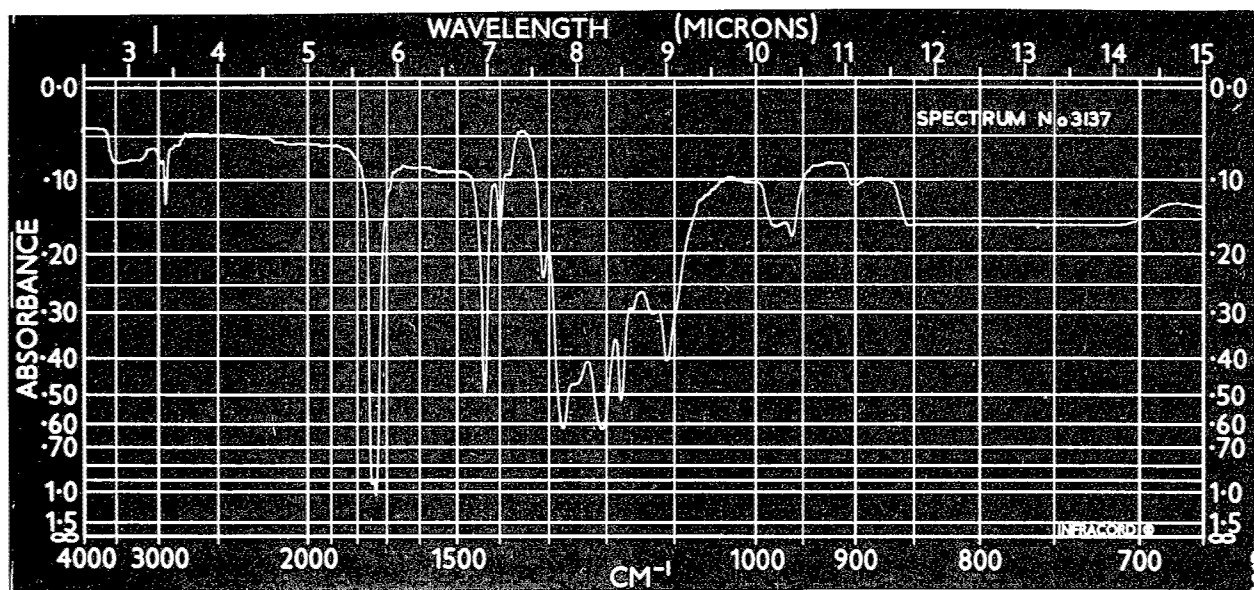
Spectrum No. 3040      3,4,3',4'-Tetraminohexafluorobiphenyl  
(KBr disc)



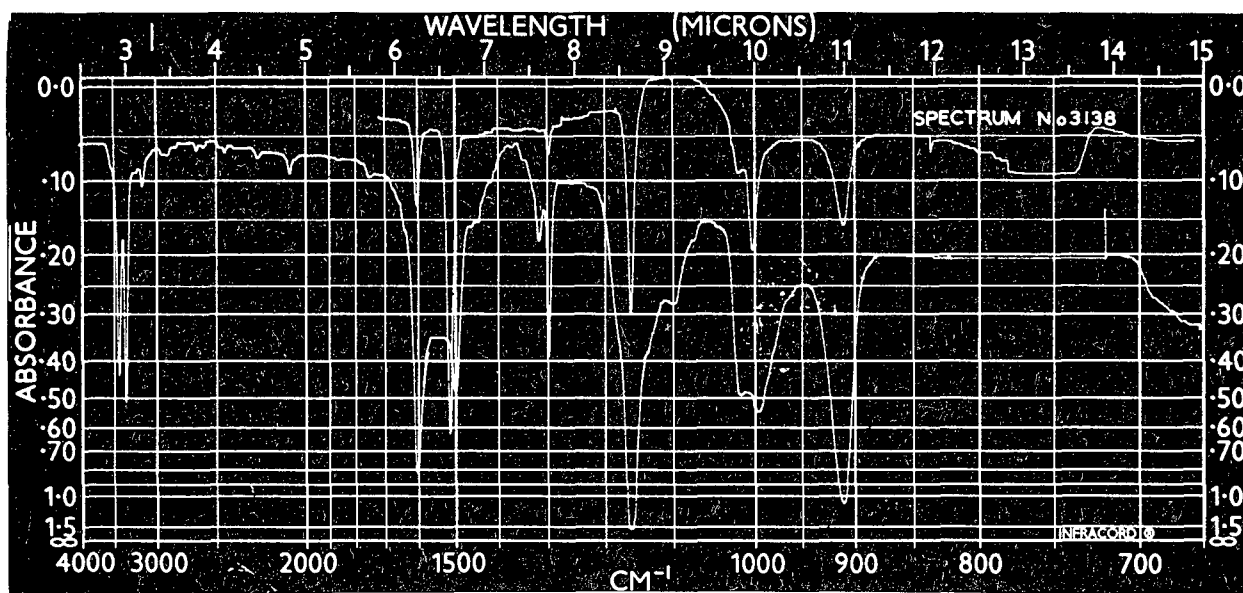
Spectrum No. 3075      Tetrafluororesorcinol (KBr disc)



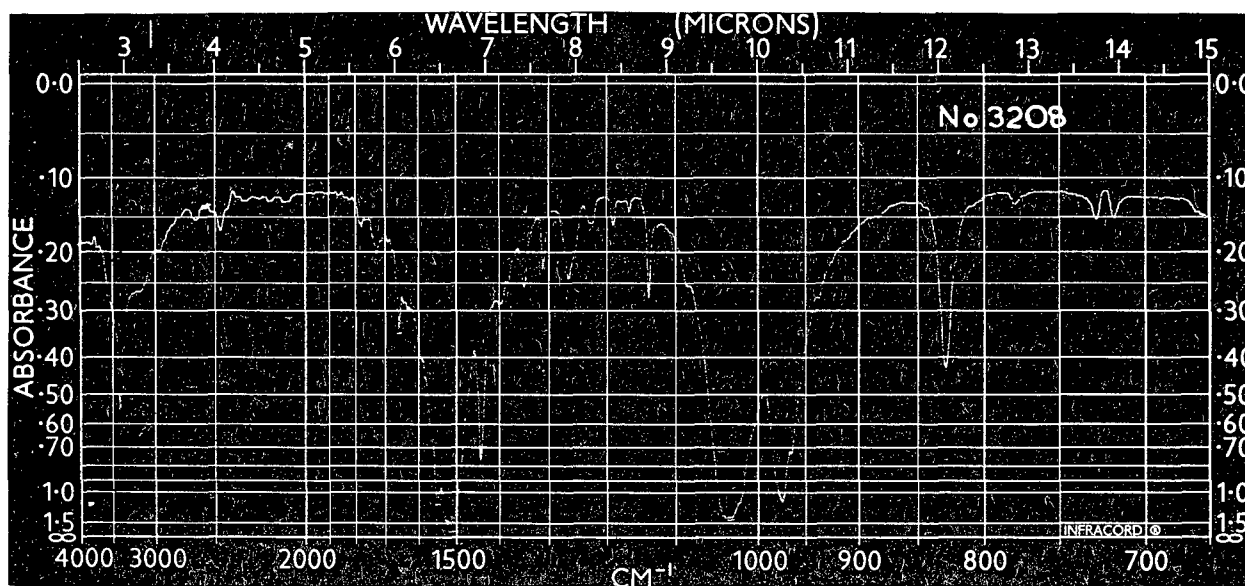
Spectrum No. 3076 Tetrafluororesorcinol (in CCl<sub>3</sub>CN)



Spectrum No. 3137 Tetramethyl dichloropyromellitate  
(in CCl<sub>4</sub>)

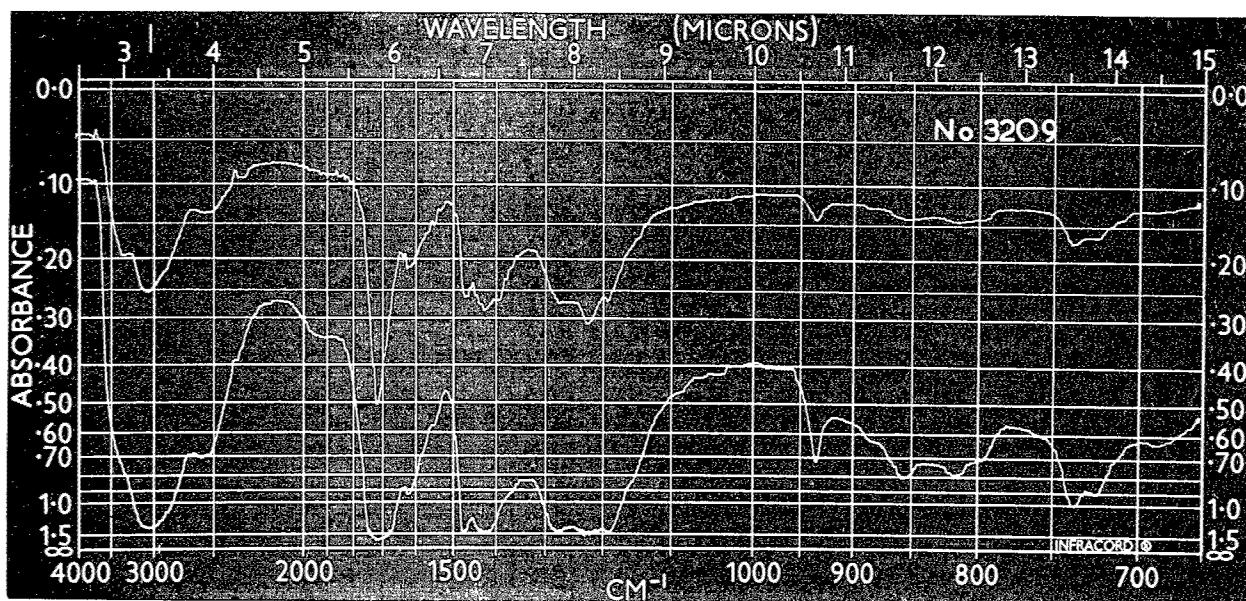


Spectrum No. 3138      Tetrafluoro-p-phenylenediamine (in  $\text{CCl}_4$ )

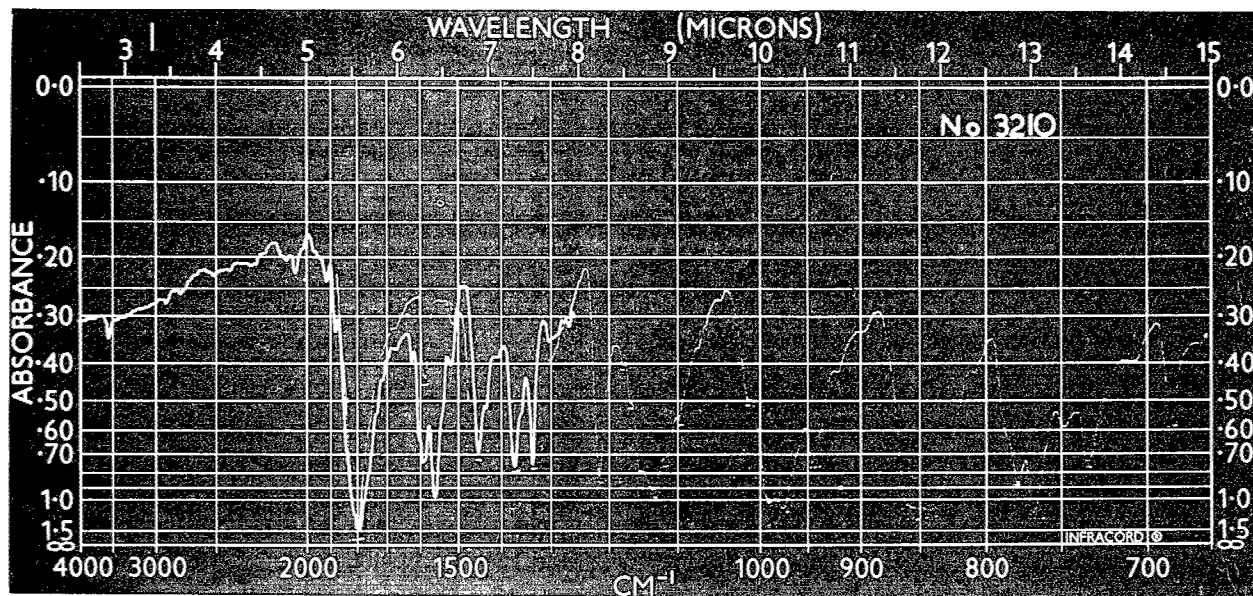


Spectrum No. 3208      Decafluorodiphenylamine (KBr disc)



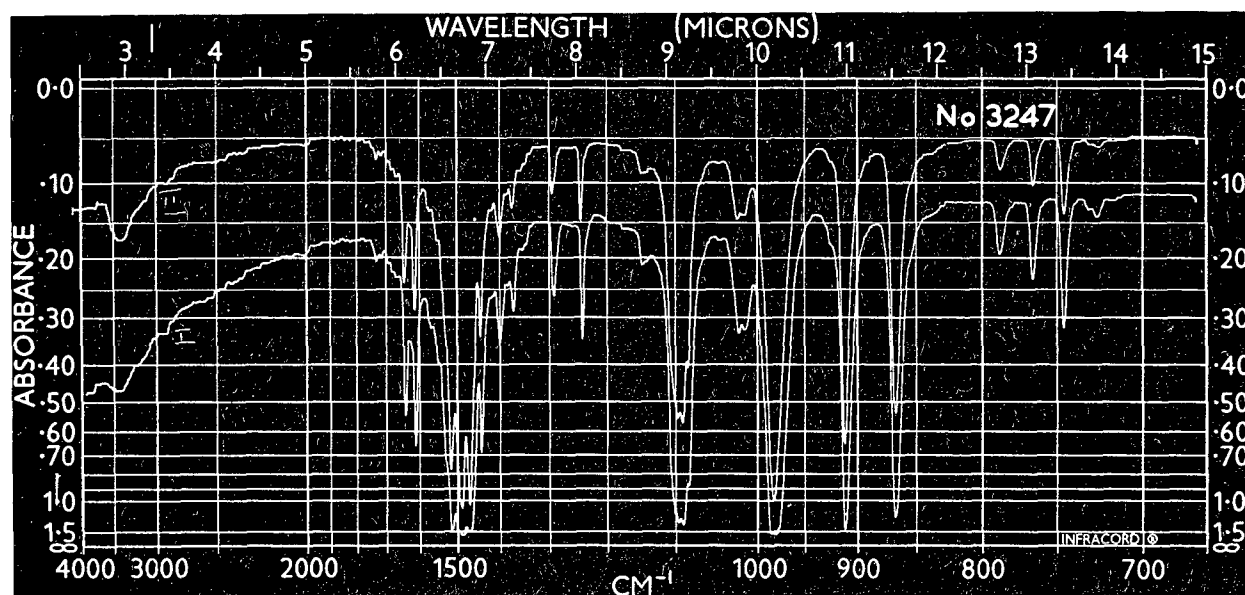


Spectrum No. 3209      Impure difluoropyromellitic acid from  
acid hydrolysis of suspected p-difluoro-  
tetracyanobenzene (KBr disc)

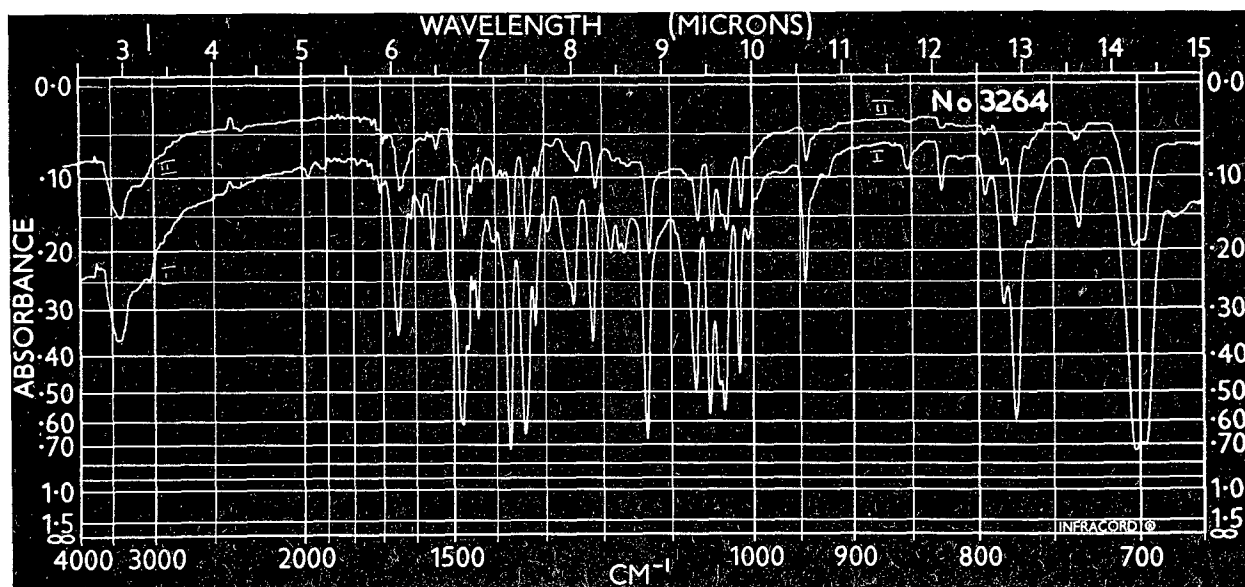


Spectrum No. 3210      Dichloropyromellitoylchloride (Nujol  
and hexachlorobutadiene mulls)

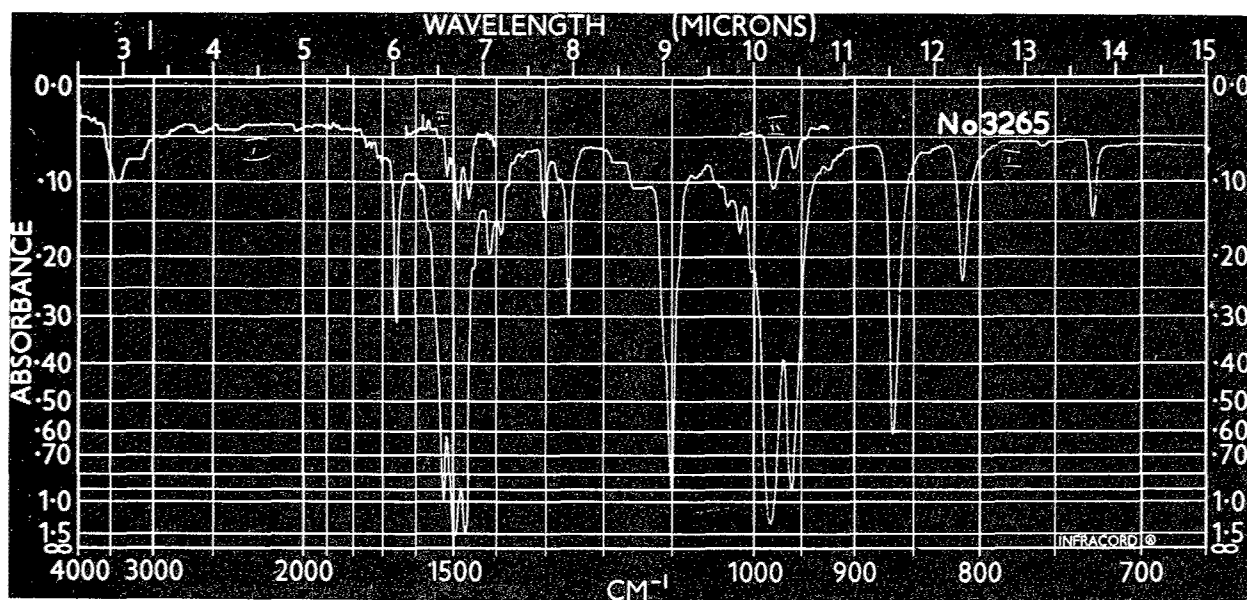




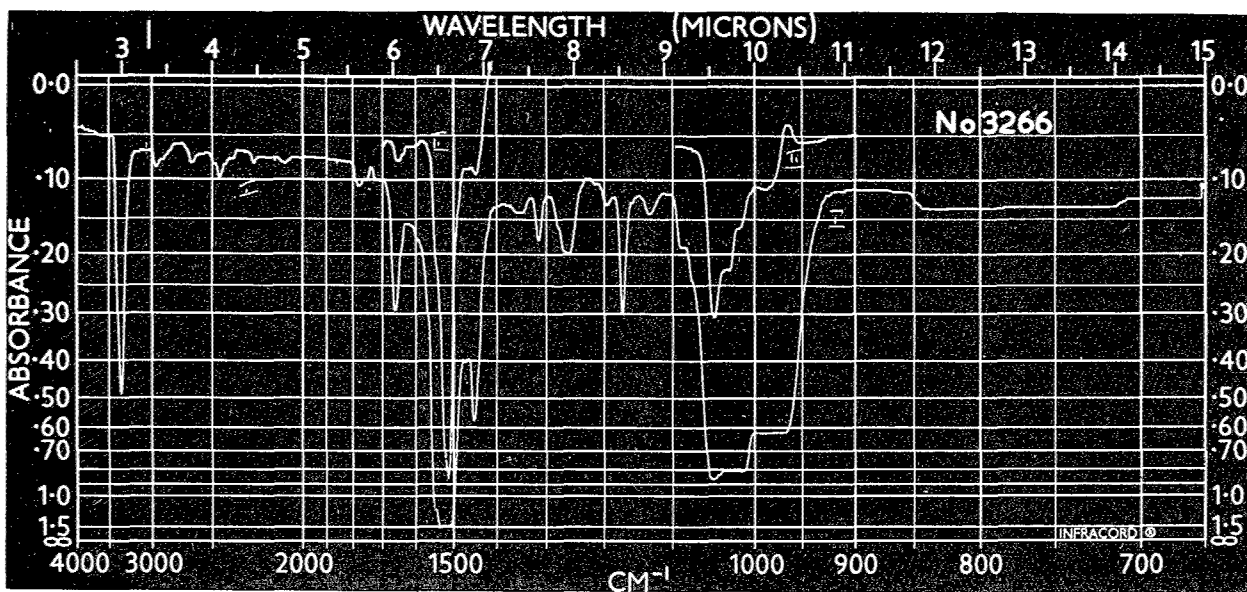
Spectrum No. 3247     1,3-Bis(pentafluorophenylthio)tetrafluorobenzene (KBr disc)



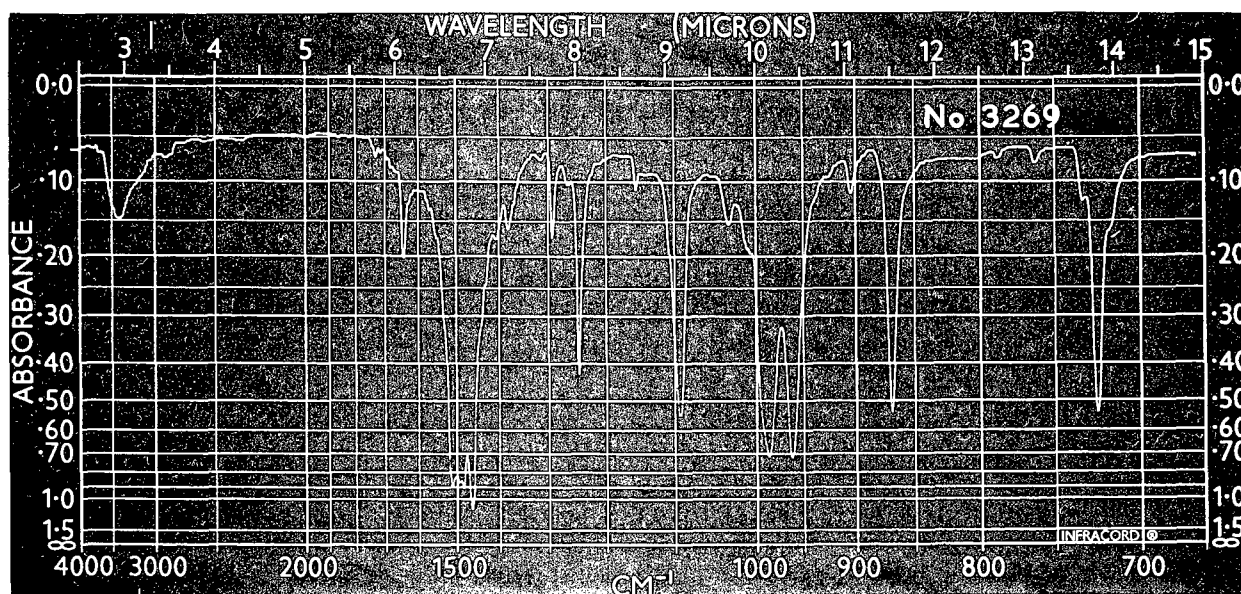
Spectrum No. 3264     6,6'-Bis(2,3-diphenyl-5,7,8-trifluoroquinoxalyl) (KBr disc)



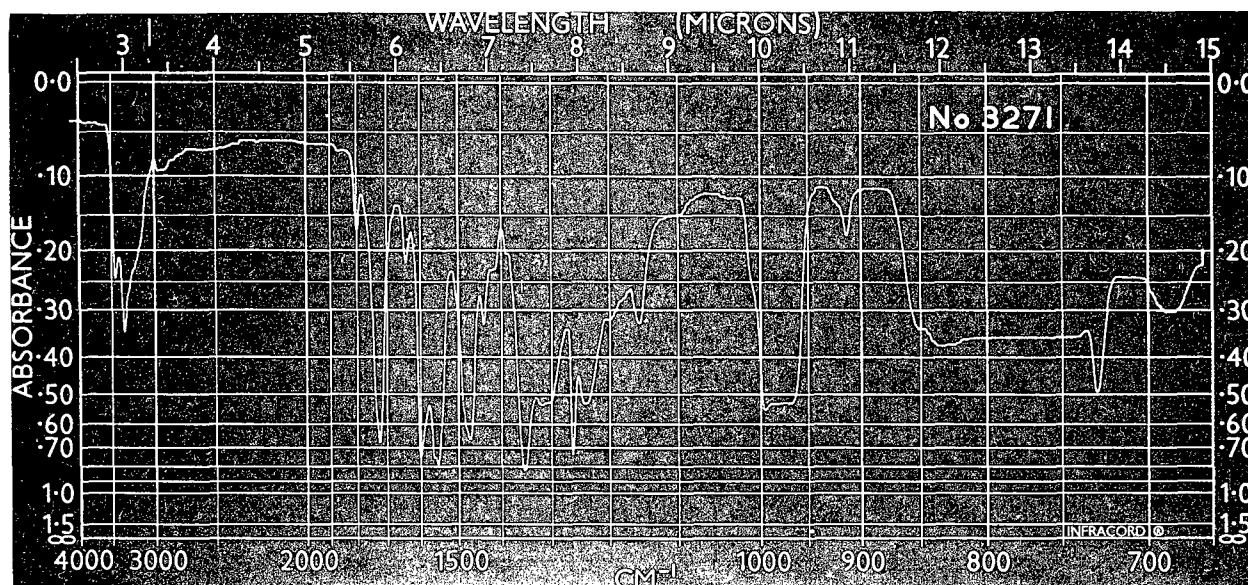
Spectrum No. 3265     1,4-Bis(pentafluorophenylthio)tetrafluorobenzene (KBr disc)



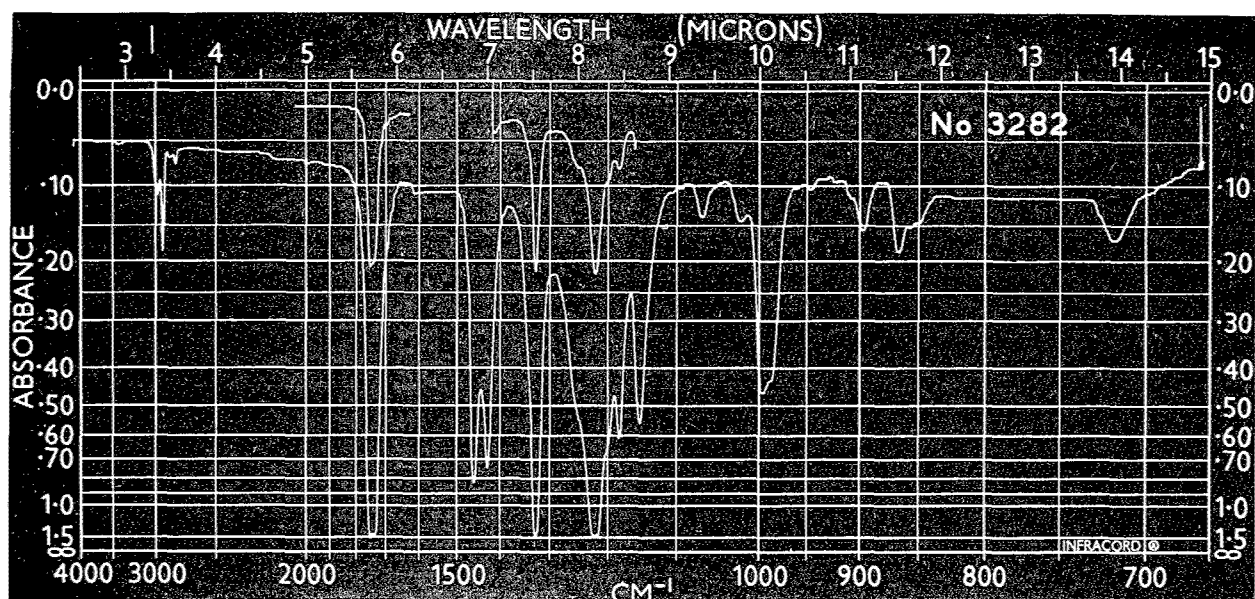
Spectrum No. 3266     1,4-Bis(pentafluoroanilino)tetrafluorobenzene (in CCl<sub>3</sub>CN)



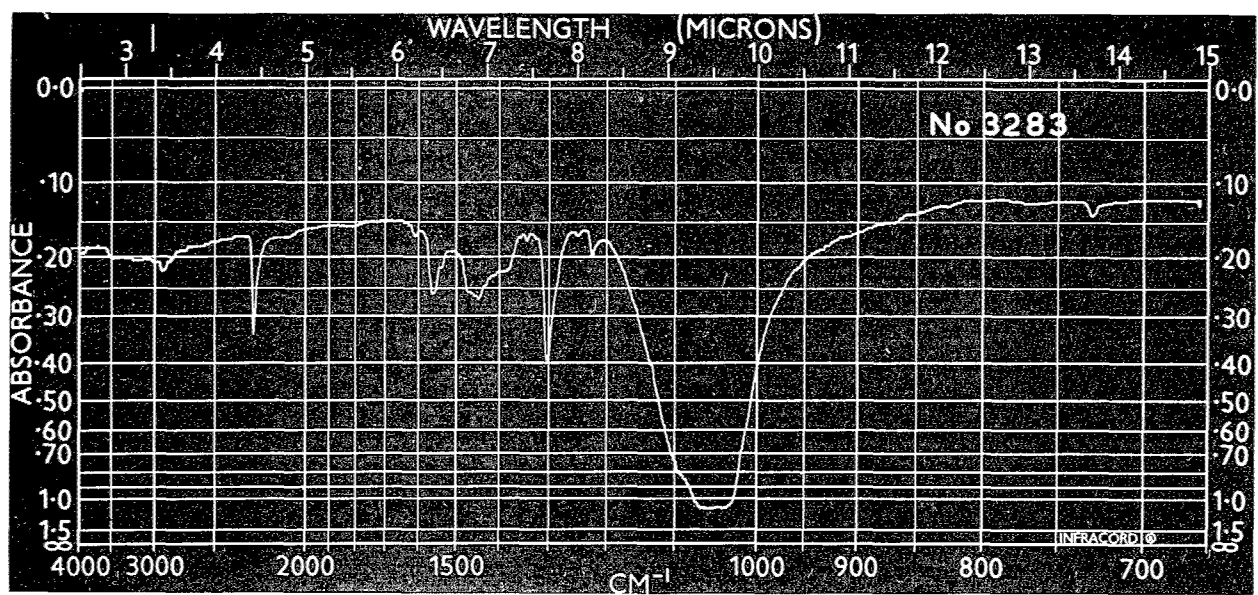
Spectrum No. 3269      4,4'-Bis(pentafluorophenylthio)octafluoro-  
biphenyl (KBr disc)



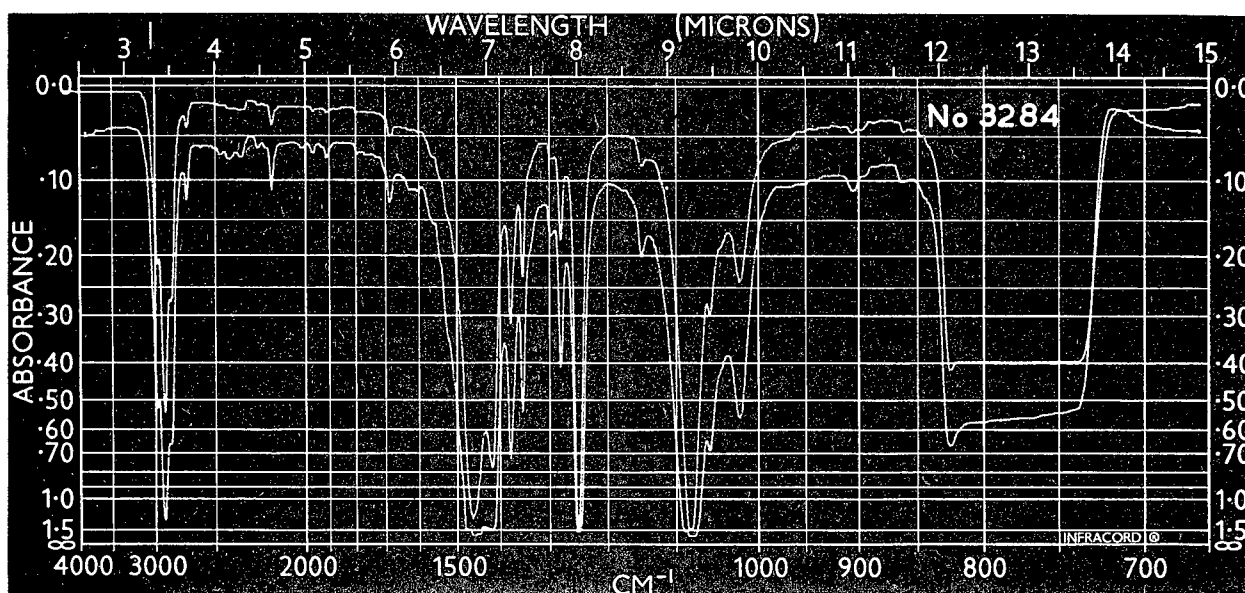
Spectrum No. 3271      3,3'-Dihydroxy-4,4'-dinitrohexafluoro-  
biphenyl (in CCl<sub>3</sub>CN)



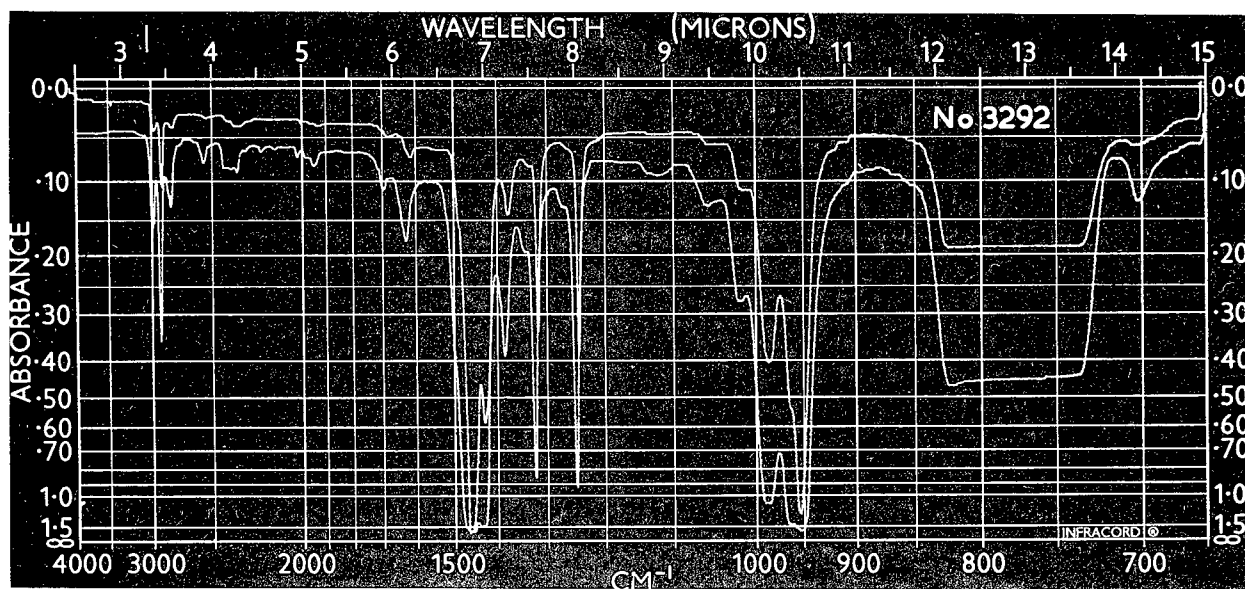
Spectrum No. 3282 Tetramethyl difluoropyromellitate (KBr disc)



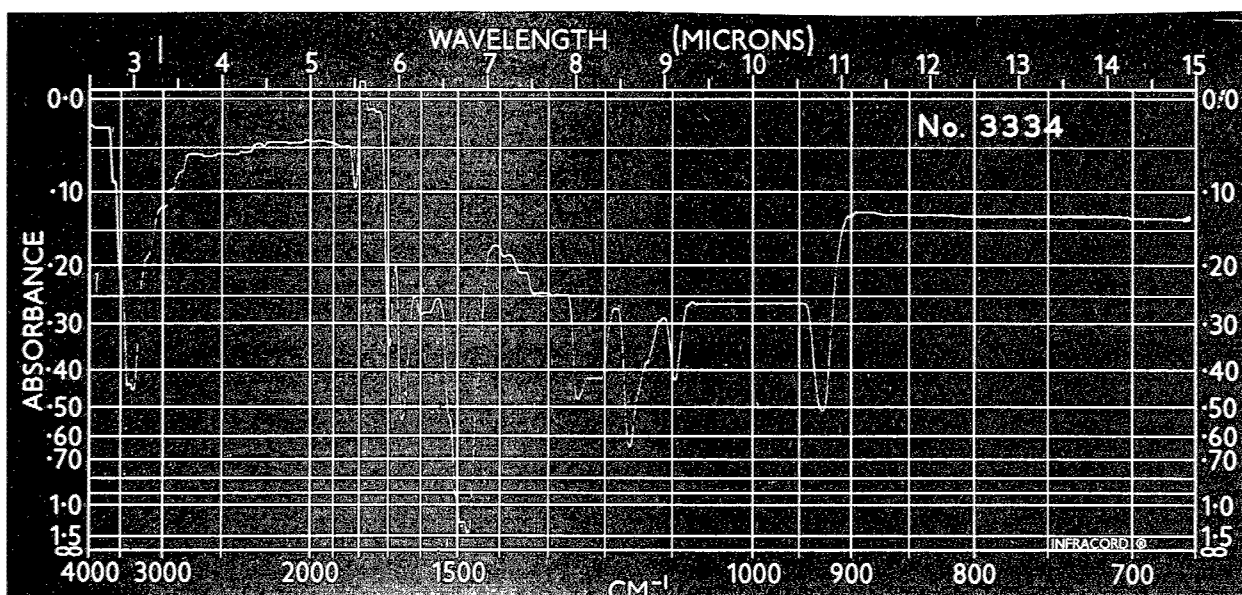
Spectrum No. 3283 4-Fluorodurenediazonium borofluoride (film)



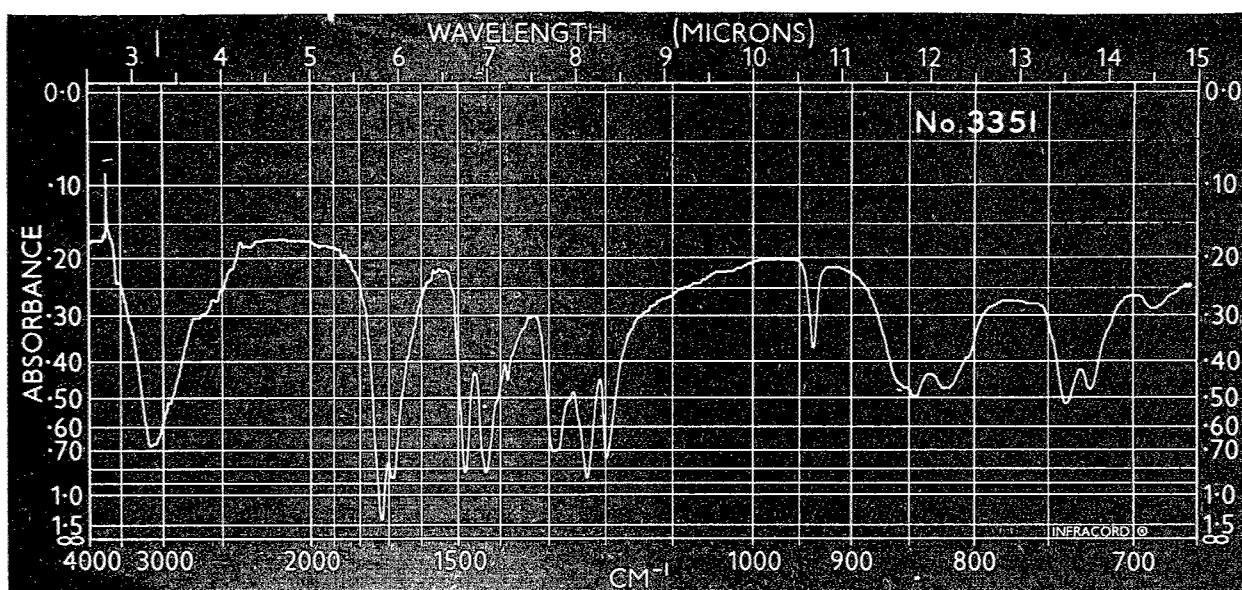
Spectrum No. 3284      Difluorodurene (in CCl<sub>4</sub>)



Spectrum No. 3292      1,4-Bis(methylthio)tetrafluorobenzene  
(in CCl<sub>4</sub>)

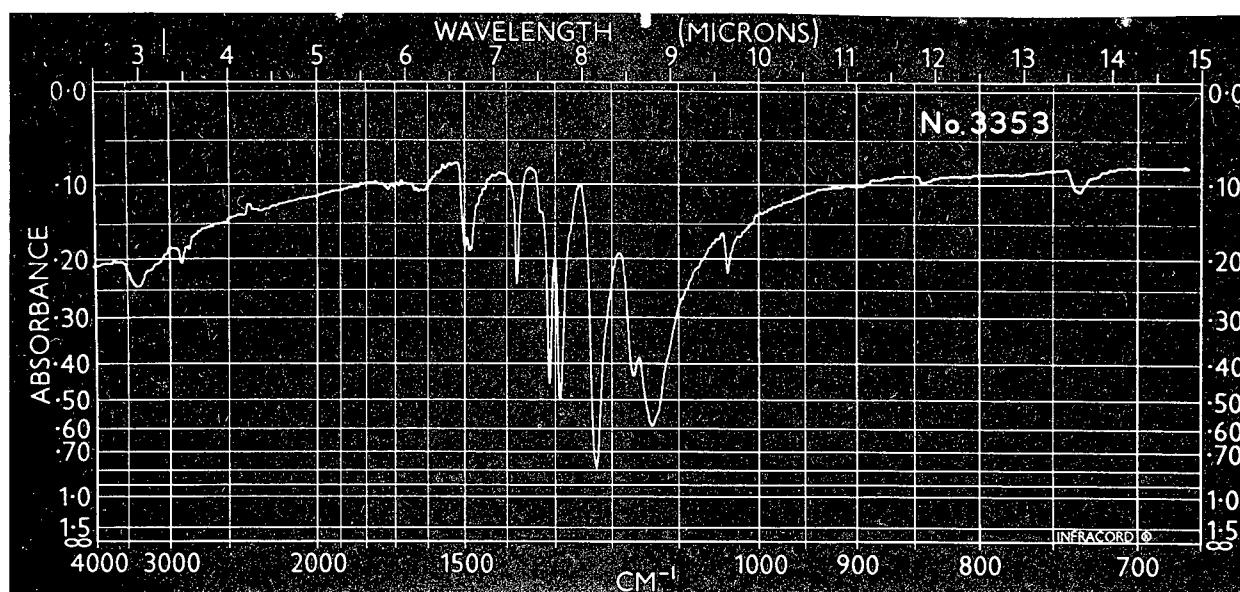


Spectrum No. 3334     3,3'-Dihydroxy-4,4'-diaminohexafluoro-  
biphenyl (in CCl<sub>3</sub>CN)

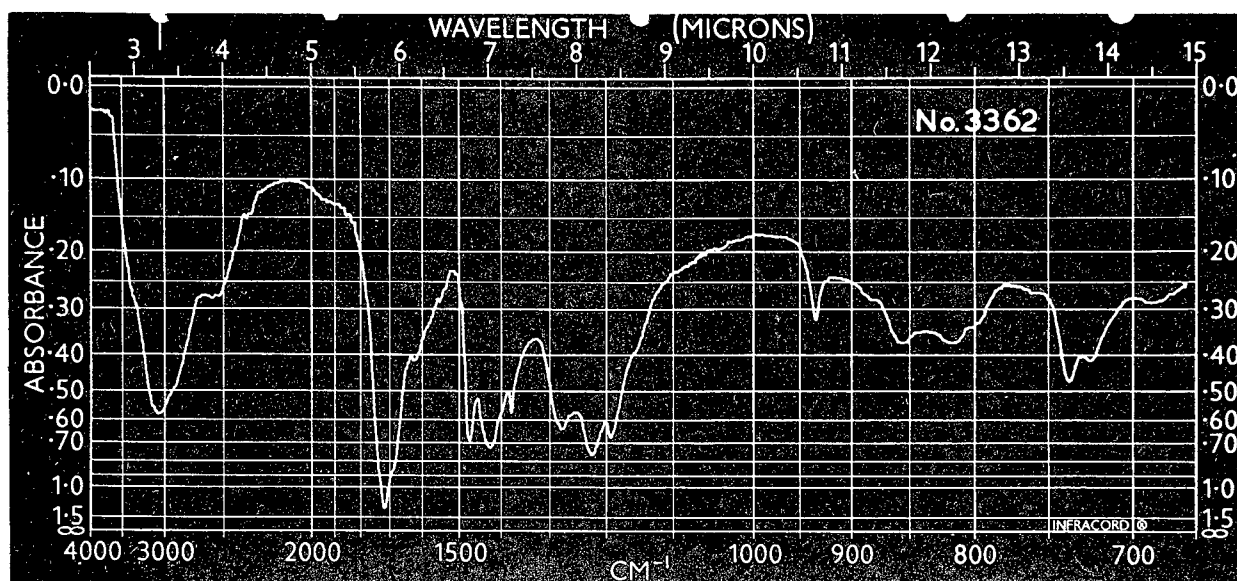


Spectrum No. 3351     Difluoropyromellitic acid (KBr disc)

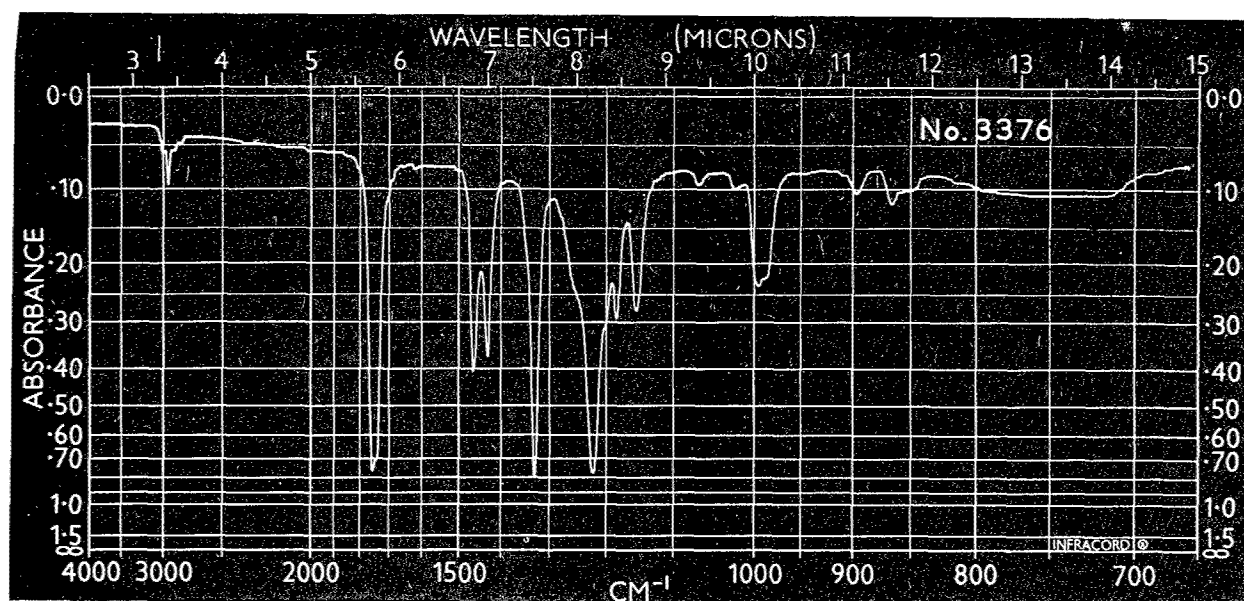




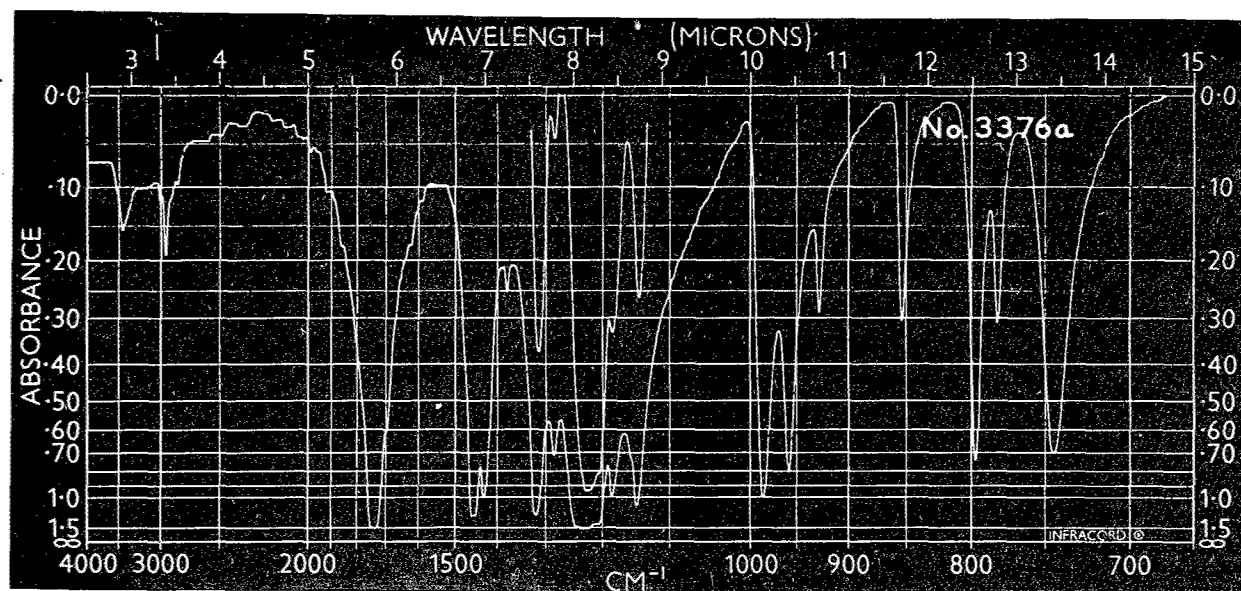
Spectrum No. 3353      Pentabromobenzotrifluoride (KBr disc)



Spectrum No. 3362      Impure difluoropyromellitic acid after  
treatment with nitrous acid (KBr disc)

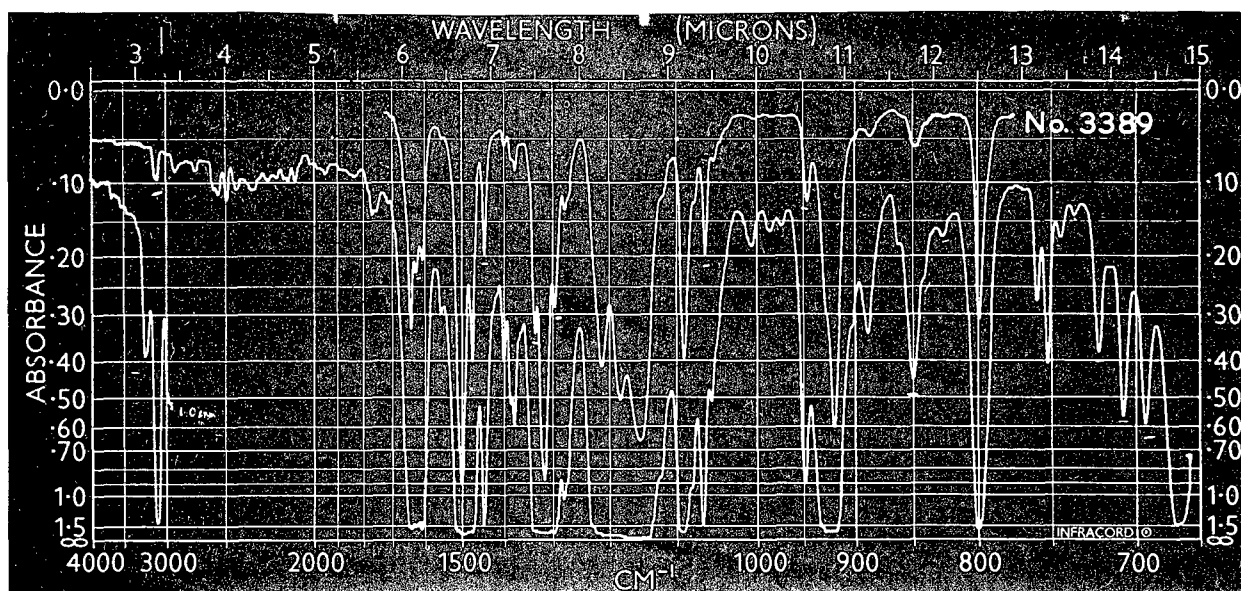


Spectrum No. 3376 Tetramethyl difluoropyromellitate (in CCl<sub>4</sub>)

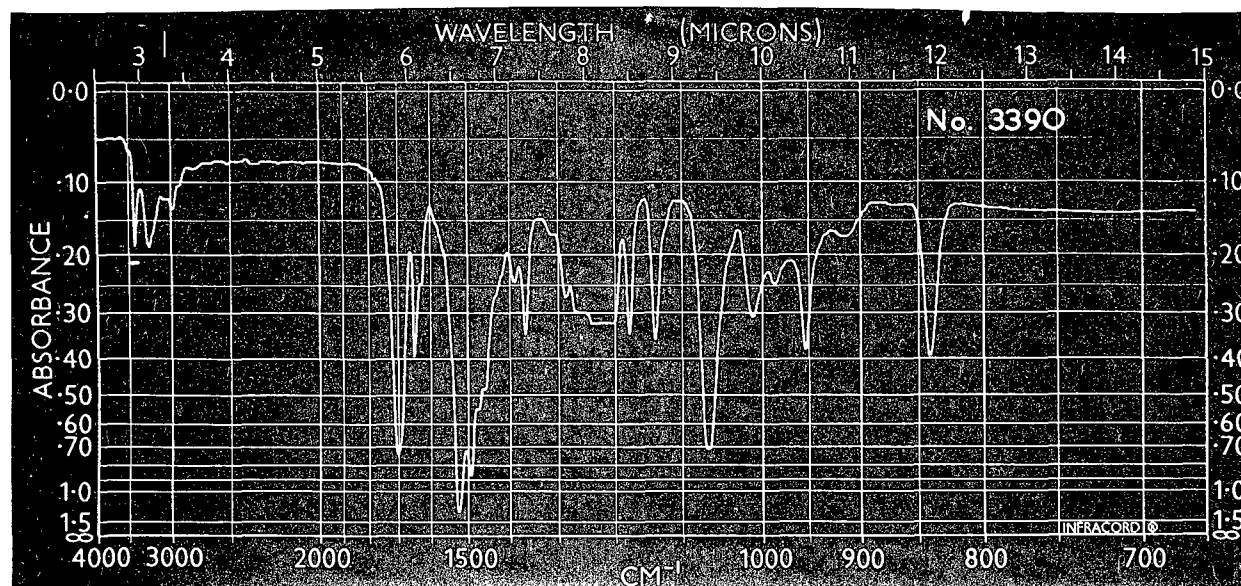


Spectrum No. 3376a Tetramethyl difluoropyromellitate (KBr disc)

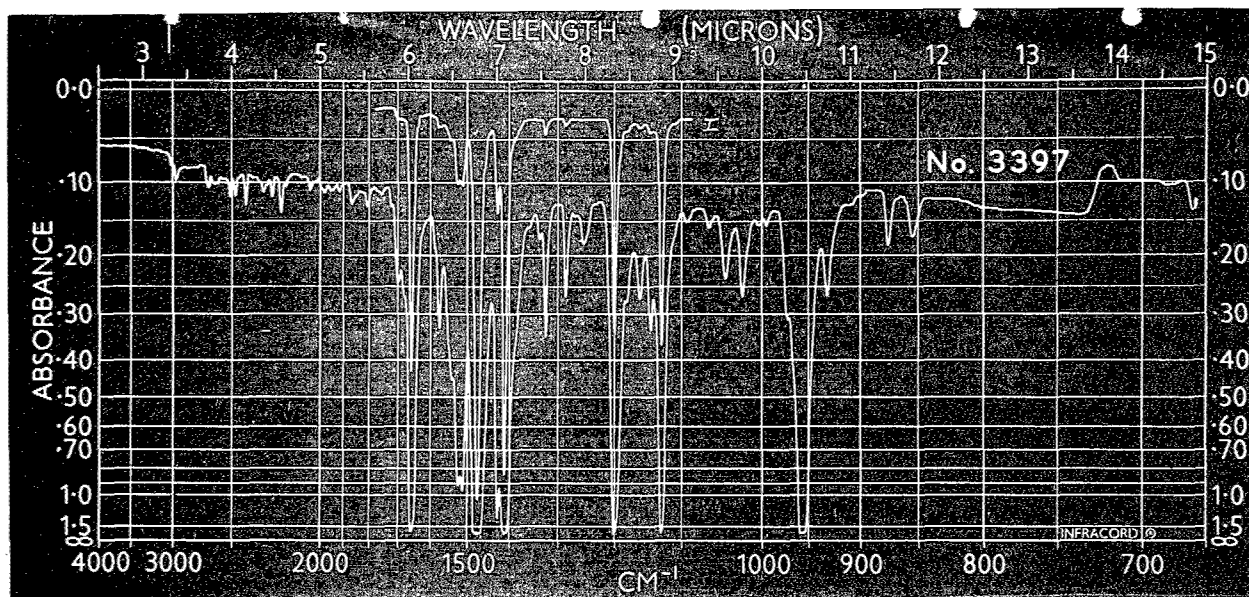




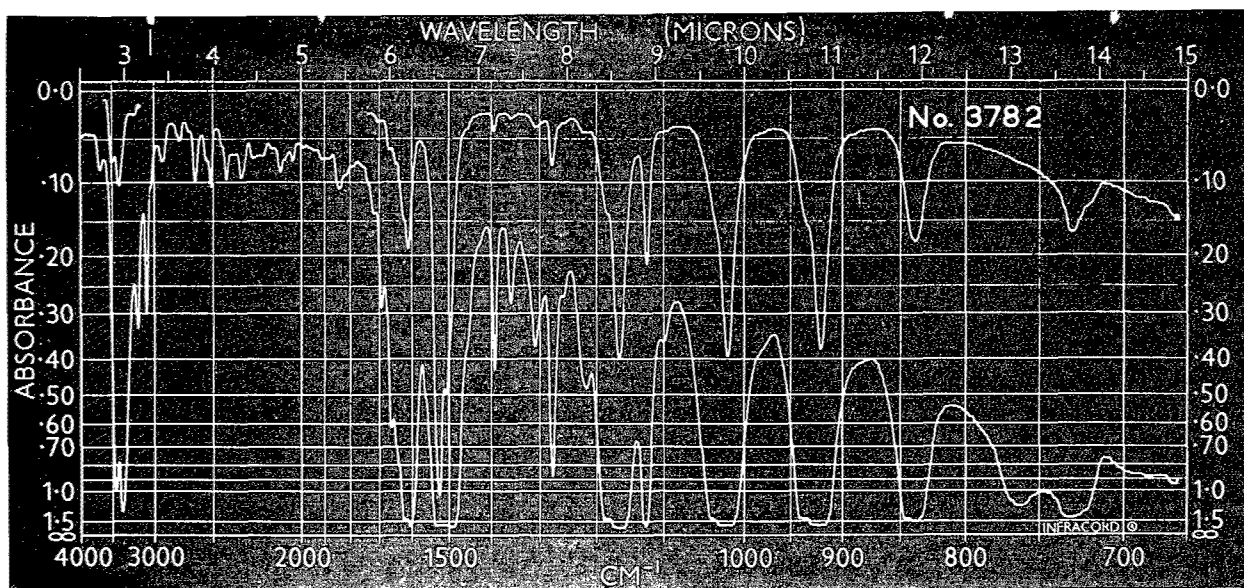
Spectrum No. 3389      Impure 3-bromoheptafluorotoluene (film)



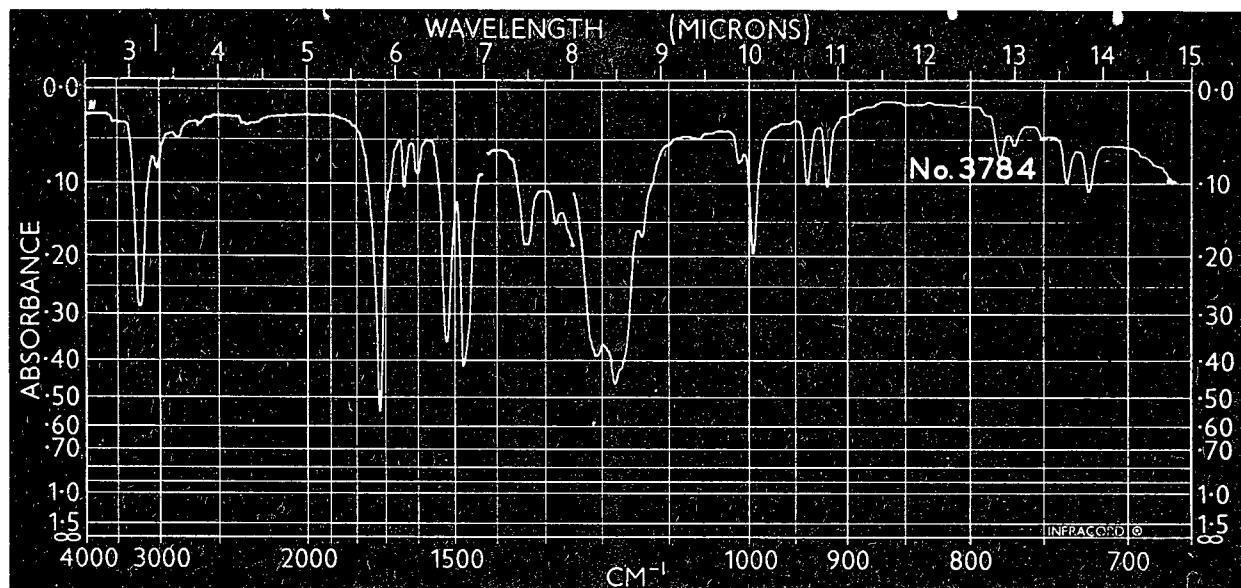
Spectrum No. 3390      2,3,4,6-Tetrafluoroacetanilide (in  $\text{CHCl}_3$ )



Spectrum No. 3397      Octafluoronaphthalene (in  $\text{CCl}_4$ )



Spectrum No. 3782      2,3,4,6-Tetrafluoroaniline (film)



Spectrum No. 3784

3,4,3',4'-Tetra(trifluoroacetimido)hexa-  
fluorobiphenyl {Kel F, hexachlorobutadiene  
and Nujol mulls}

## APPENDIX B - I.R. SPECTRA

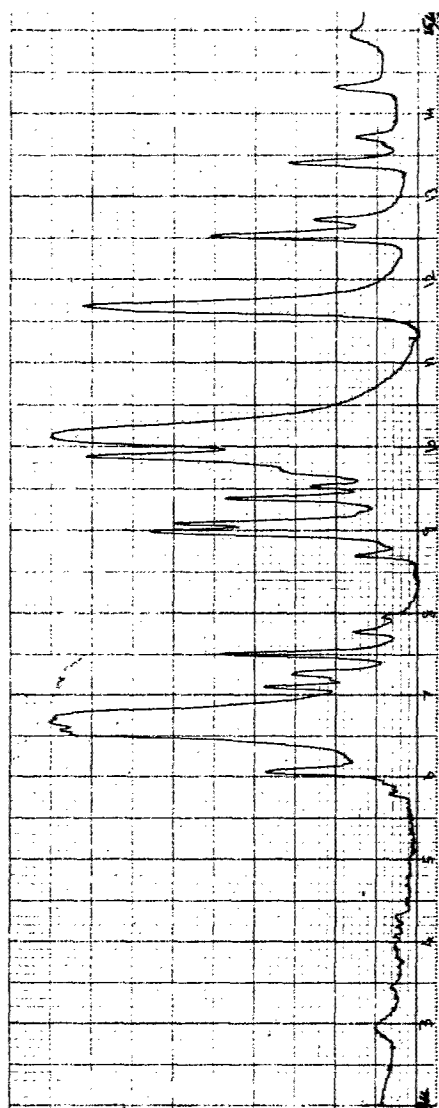
### Infra-red Spectra of new compounds and polymers described in Part II

1. 3,4,5-Tri(pentafluorophenyl)-1,2,4-triazole (KCl disc.)
2. 3,5-Di(pentafluorophenyl)-4-phenyl-1,2,4-triazole (KCl disc)
3. N-(Pentafluorophenyl)benzenesulphonamide (KCl disc)
4. 3,5-Di(pentafluorophenyl)-1,2,4-triazole (Nujol mull)
5. Decafluorobenzalazine ( $\text{CCl}_4/\text{CS}_2$  Solutions)
6.  $\alpha$ -Chlorodecafluorobenzalazine ( $\text{CCl}_4/\text{CS}_2$  Solutions)
7. Tetrafluoroisophthaloyl bis(pentafluorobenzhydrazide) (KCl disc)
8. m-Di(2-pentafluorophenyl-1,3,4-oxadiazolyl-5)tetrafluorobenzene (KCl disc)
9. Tetrafluoroterephthalhydrazide (Nujol mull)
10. Tetrafluoroterephthaloyl bis(pentafluorobenzhydrazide) (KCl disc)
11. p-Di(2-pentafluorophenyl-1,3,4-oxadiazolyl-5)tetrafluorobenzene (KCl disc)
12. Pentafluorobenzhydrazide toluene p-sulphonate (Nujol mull)
13. Phenyl pentafluorobenzoate ( $\text{CCl}_4/\text{CS}_2$  Solutions)
14. Tetrafluoroisophthalaldi(pentafluoroanilide) (Nujol mull)
15. m-Di(pentafluorobenzamido)tetrafluorobenzene (Nujol mull)
16. p-Di(tetrafluorophthalimido)tetrafluorobenzene (KCl disc)
17. Possibly o-di(tetrafluorophthalimido)tetrafluorobenzene (KCl disc)  
See page 87.
18. m-Di(tetrafluorophthalimido)tetrafluorobenzene (KCl disc)
19. p-Di(pentafluorobenzamido)tetrafluorobenzene (KCl disc)
20. N,N,N',N'-Tetra(pentafluorophenyl)tetrafluoroterephthaldiamide (KCl disc)

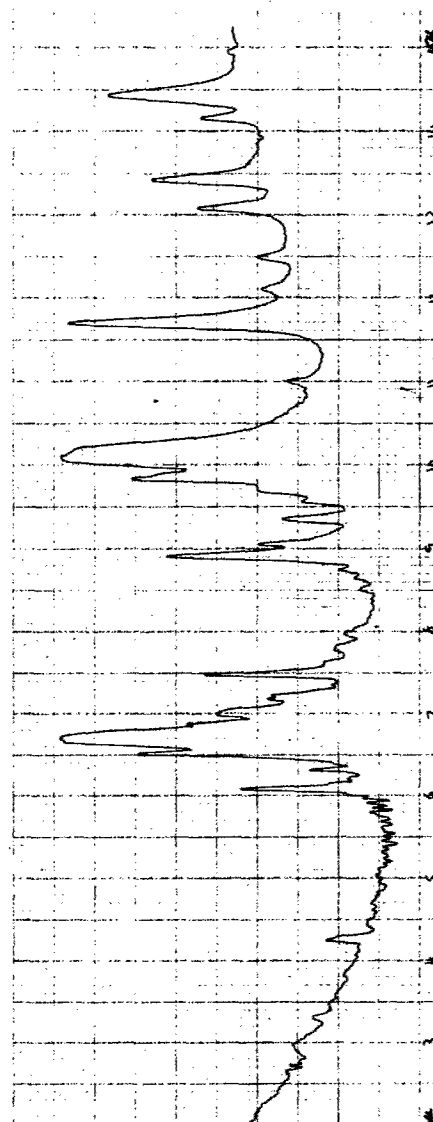
APPENDIX B - I.R. SPECTRA (Contd.)

Infra-red Spectra of new compounds and polymers described in Part II

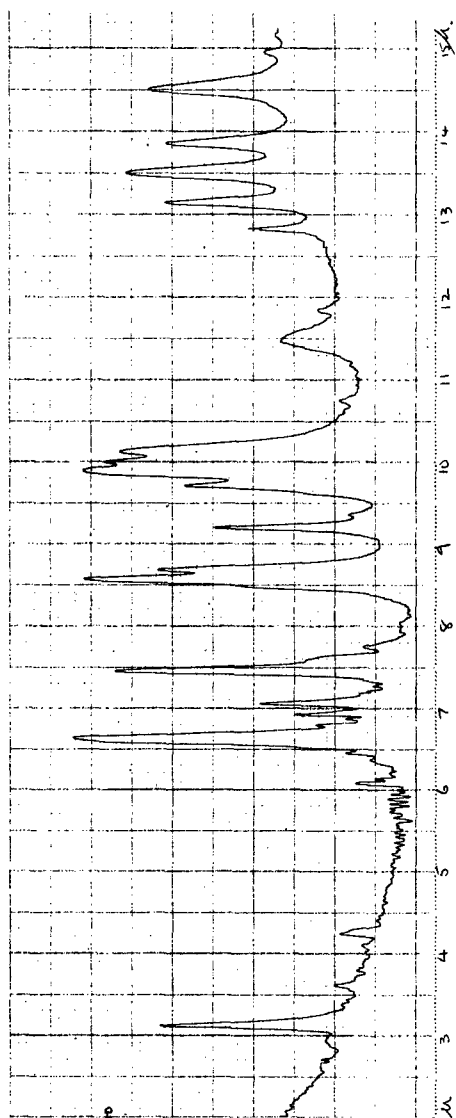
21. Di(pentafluorophenyl)octafluoro-4,4'-biphenylene biscarbonate (KCl disc)
22. Di(pentafluorophenyl)tetrafluoro-m-phenylene biscarbonate (KCl disc)
23. 1,3-Di(pentafluorobenzoyloxy)tetrafluorobenzene (KCl disc)
24. Di(pentafluorophenyl)tetrafluoroisophthalate (solution in CCl<sub>4</sub>, 2-7.5 ; CS<sub>2</sub> 7.5-15 )
25. Pentafluorophenyl chloroformate (Film)
26. Pentafluorophenylsulphenyl chloride (Film)
27. Poly(tetrafluoro-m-phenylenetetrafluoroterephthalamide) (KCl disc)
28. Poly(m-phenylene terephthalamide) (KCl disc)
29. Poly(octafluoro-4,4'-biphenylenetetrafluoroisophthalate) (KCl disc)
30. Poly(4,4'-biphenylene isophthalate) (Nujol mull)
31. Poly(octafluoro-4,4'-biphenylene tetrafluoroterephthalate) (KCl disc)
32. Poly(4,4'-biphenylene terephthalate) (Nujol mull)
33. Poly(octafluoro-4,4'-biphenylene carbonate) - preparation (a), page 100 (Fluorolube mull)
34. Poly(p-phenylenepyromellitimide) (KCl disc)
35. Poly[ (tetrafluoro-p-phenylene)pyromellitimide ] (Nujol mull)
36. Poly(isophthalhydrazide) - preparation (a), page 105 (KCl disc)
37. Poly[ 2-(m-phenylene)-1,3,4-oxadiazolyl-5 ] (KCl disc) - preparation (a), p.105
38. Poly(tetrafluorophenylene sulphide). (Nujol mull)



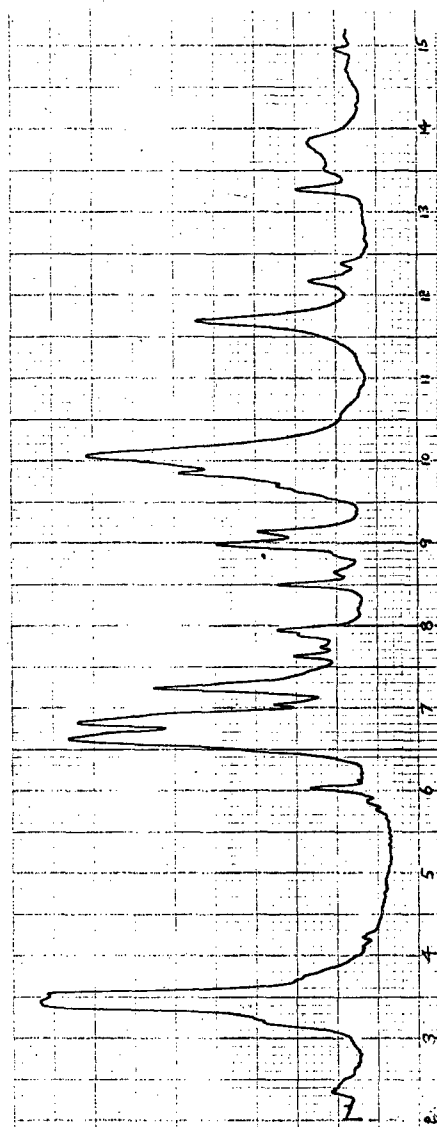
3,4,5-Tri(pentafluorophenyl)-1,2,4-triazole (KCl disc)



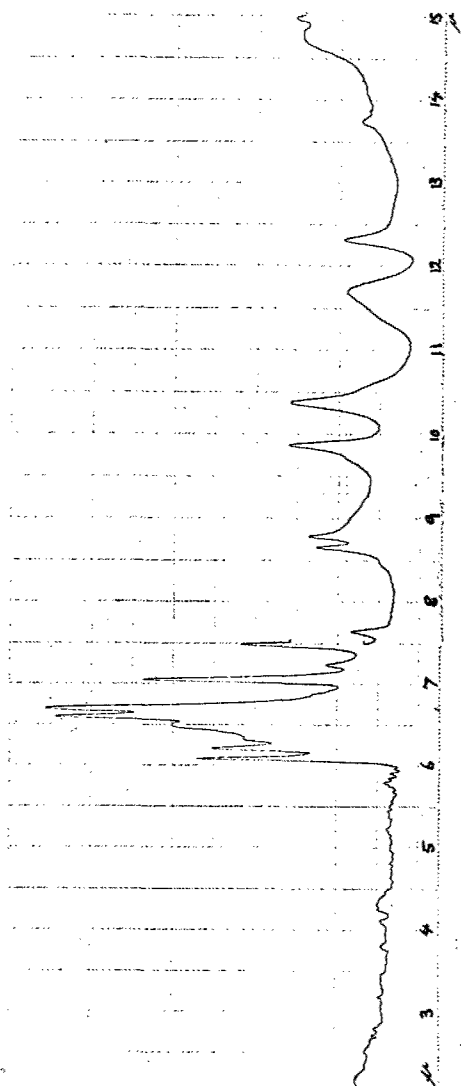
3,5-Di(pentafluorophenyl)-4-phenyl-1,2,4-triazole (KCl disc)



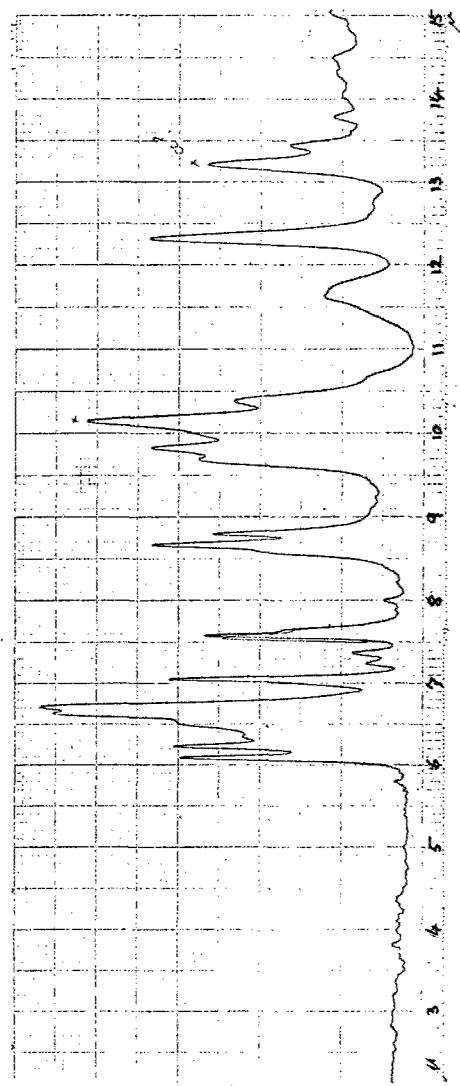
N-(Pentafluorophenyl)benzenesulphonamide (KCl disc)



3,5-Di(pentafluorophenyl)-1,2,4-triazole (Nujol mull)

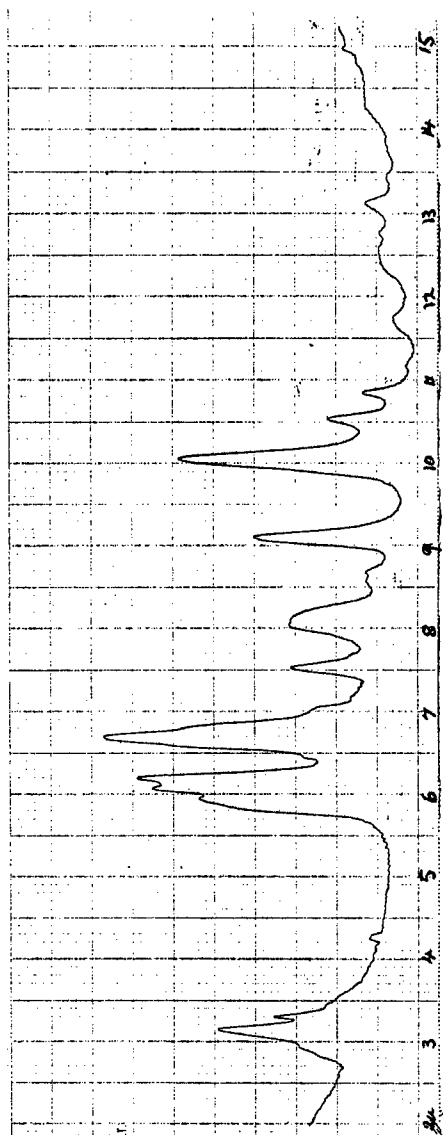


Decafluorobenzalazine ( $\text{CCl}_4/\text{CS}_2$  Solutions)

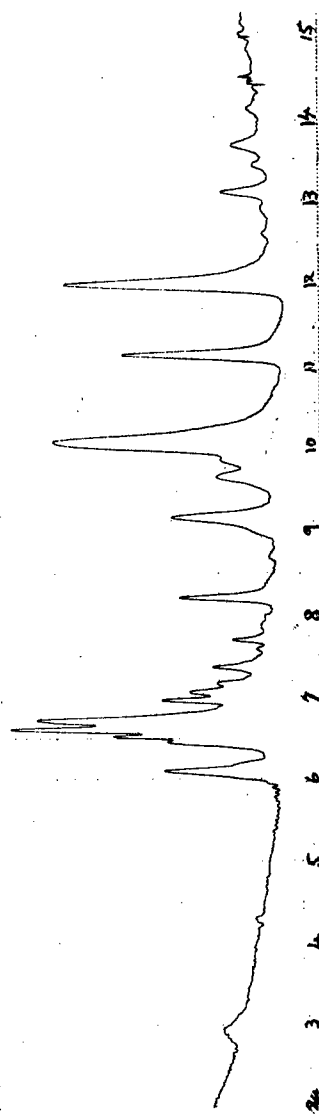


$\alpha$ -Chlorodecafluorobenzalazine ( $\text{CCl}_4/\text{CS}_2$  Solutions)

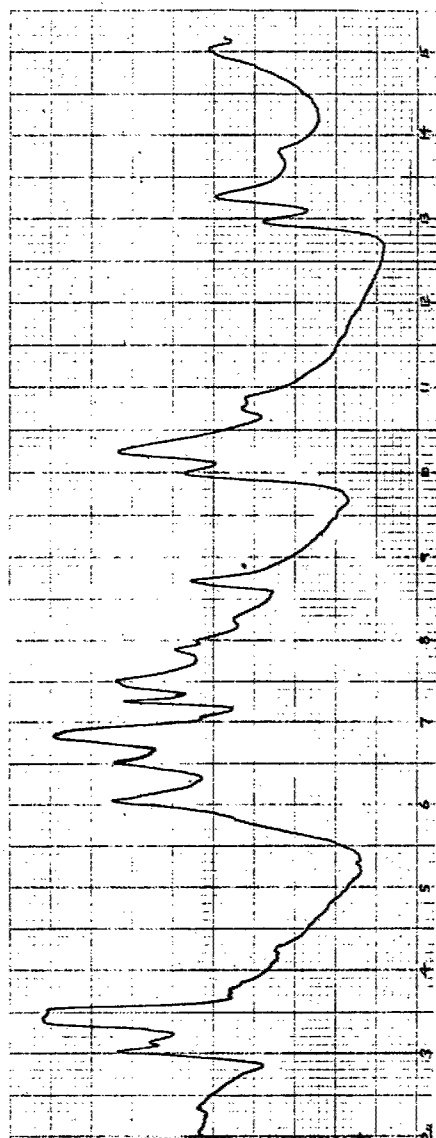




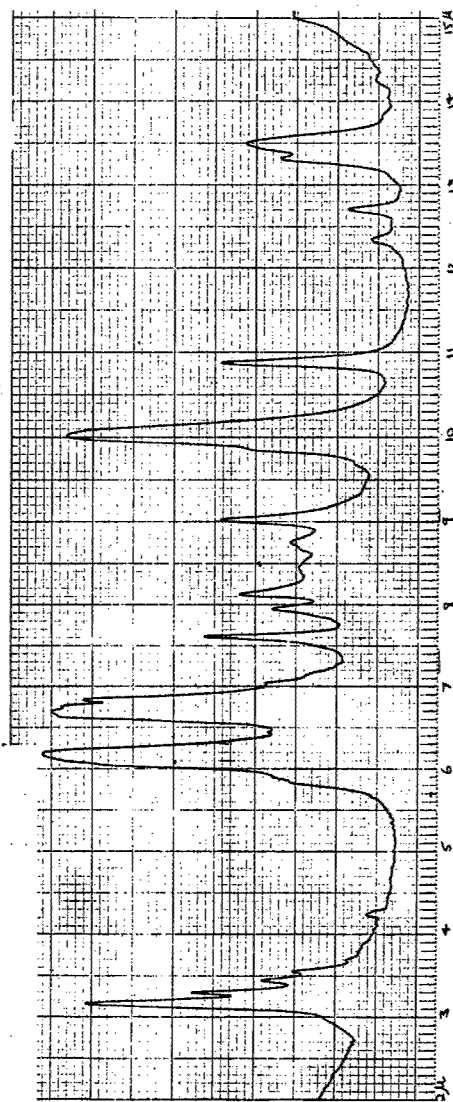
Tetrafluorisophthaloyl bis(pentafluorobenzhydrazone) (KCl disc)



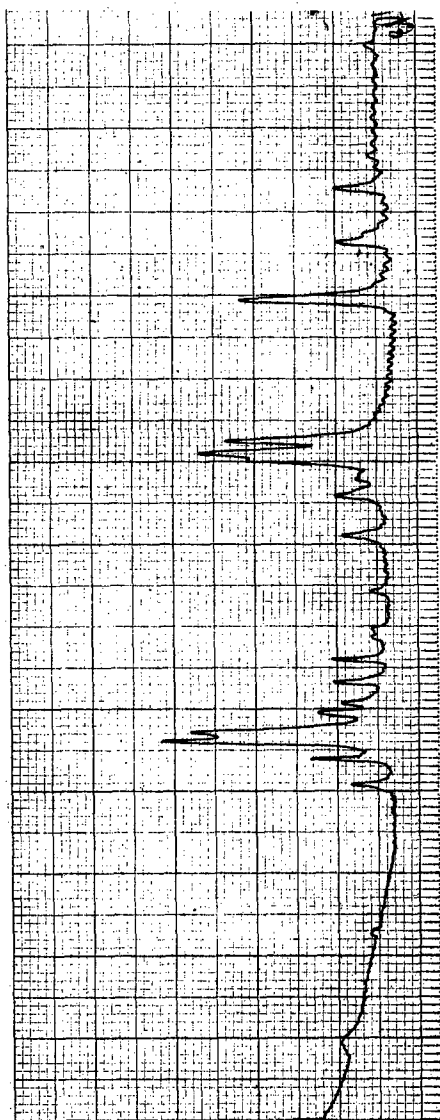
m-DI(2-pentafluorophenyl-1,3,4-oxadiazolyl-5)tetrafluorobenzene  
(KCl disc)



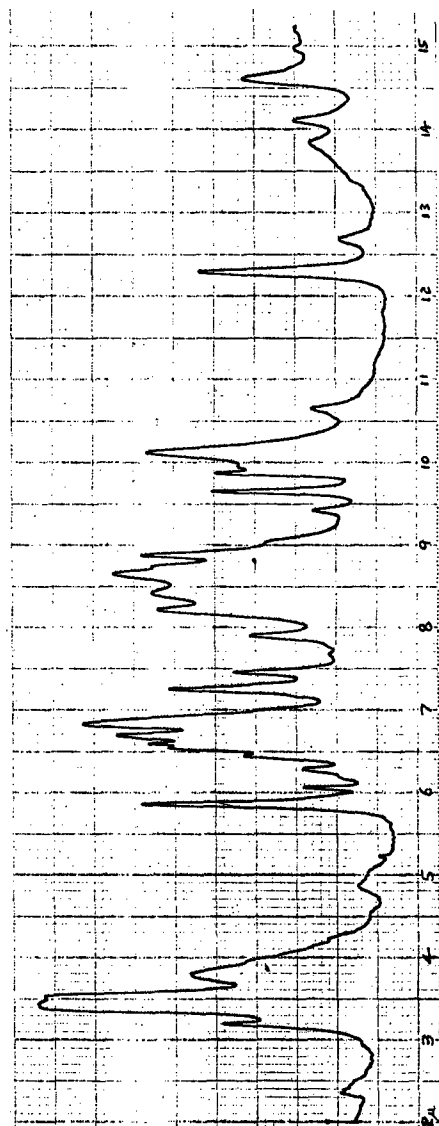
Tetrafluoroterephthalhydrazide (Nujol mull)



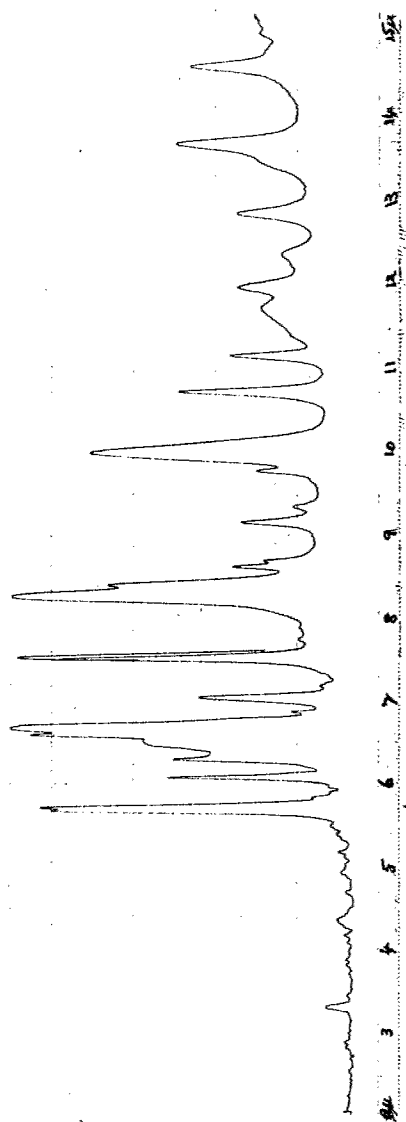
Tetrafluoroterephthaloyl bis(pentafluorobenzhydrazide) (KCl disc)



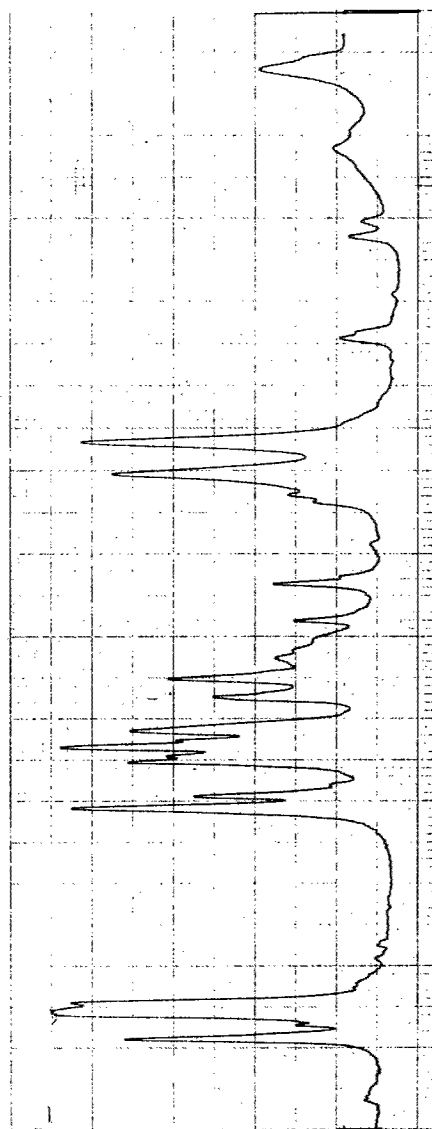
p-Di(2-pentafluorophenyl-1,3,4-oxadiazolyl-5)tetrafluorobenzene  
(KCl disc)



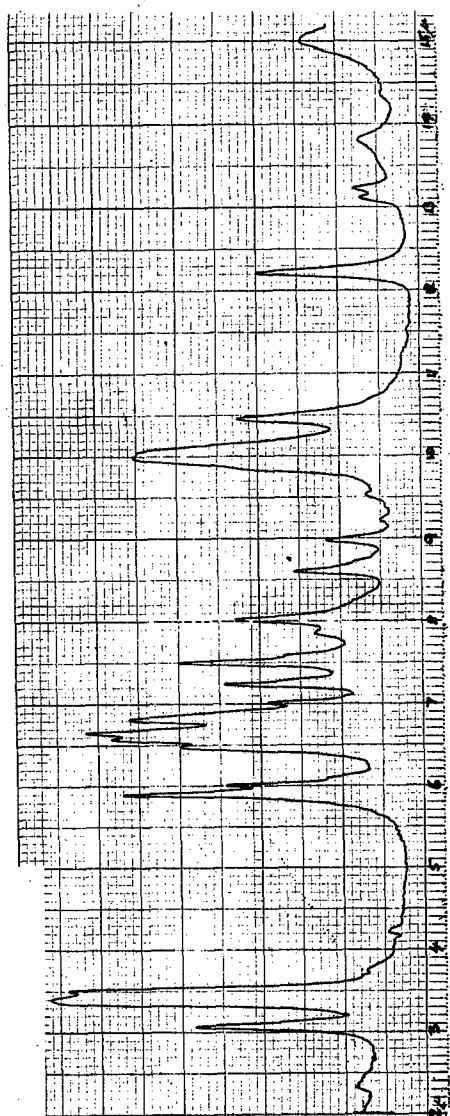
Pentafluorobenzhydrazide toluene p-sulphonate (Nujol mull)



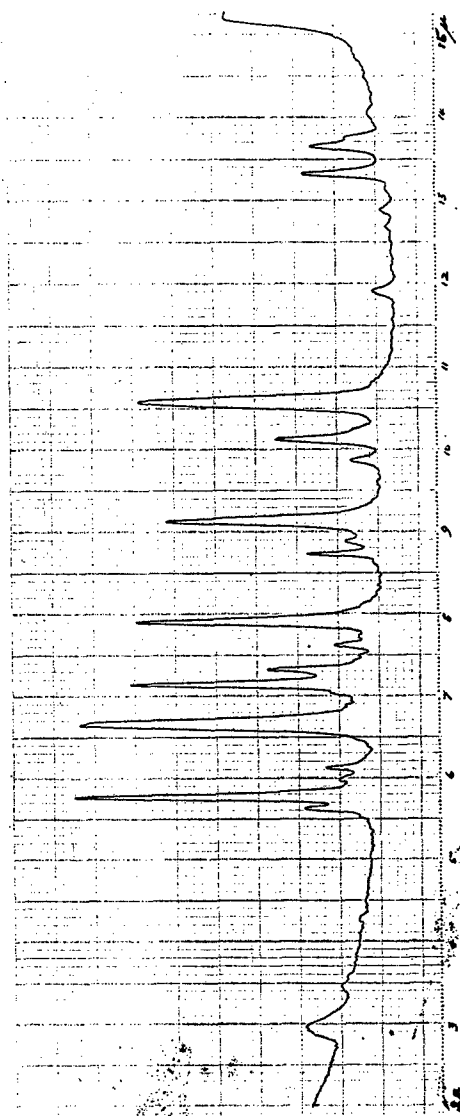
Phenyl pentafluorobenzoate. ( $\text{CCl}_4/\text{CS}_2$  Solutions)



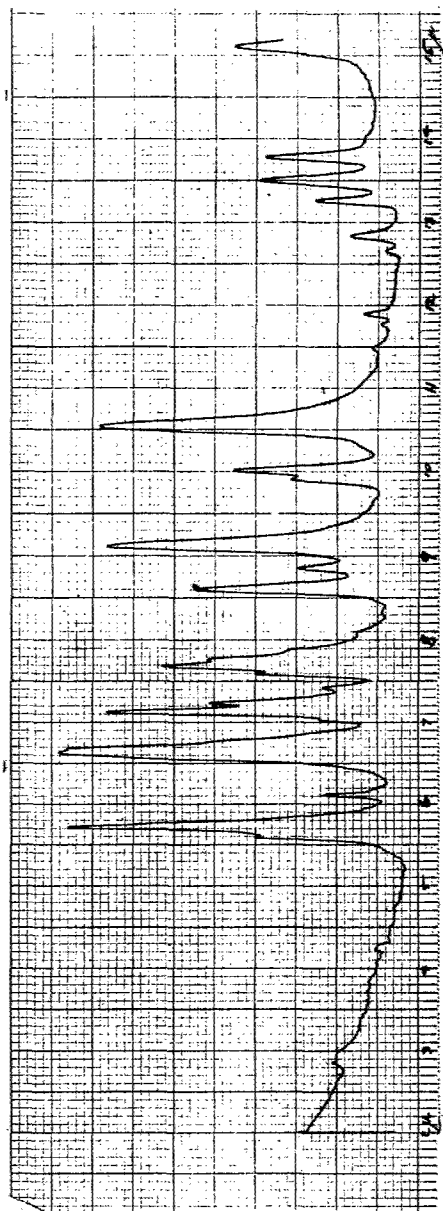
Tetrafluoroisophthaldi(pentafluoroanilide) (Nujol mull)



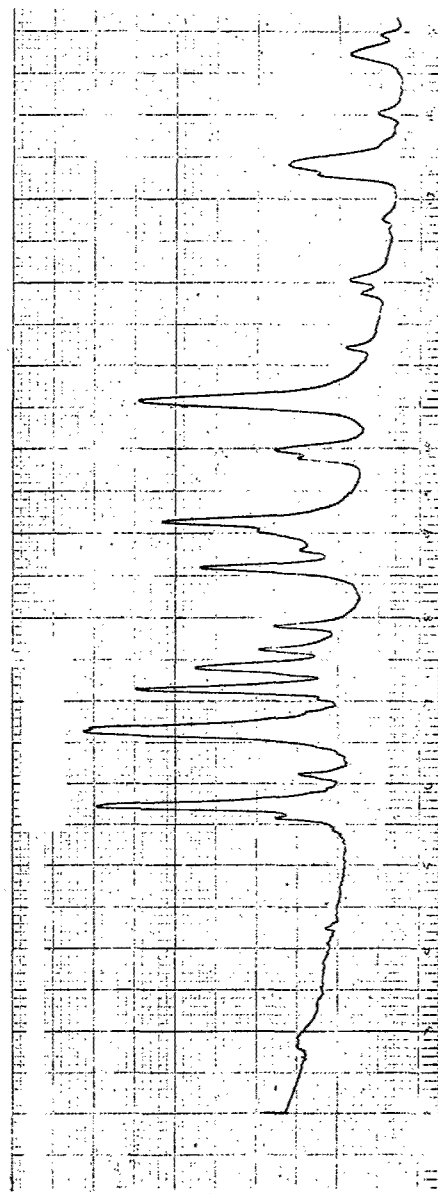
m-D1 (pentafluorobenzamido)tetrafluorobenzene (Nujol mull)



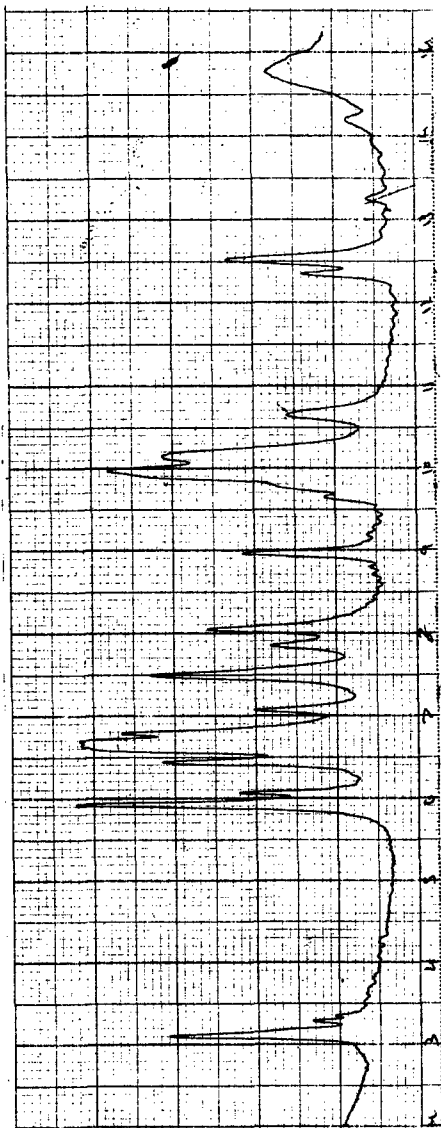
p-D1 (tetrafluorophthalimido)tetrafluorobenzene (KCl disc)



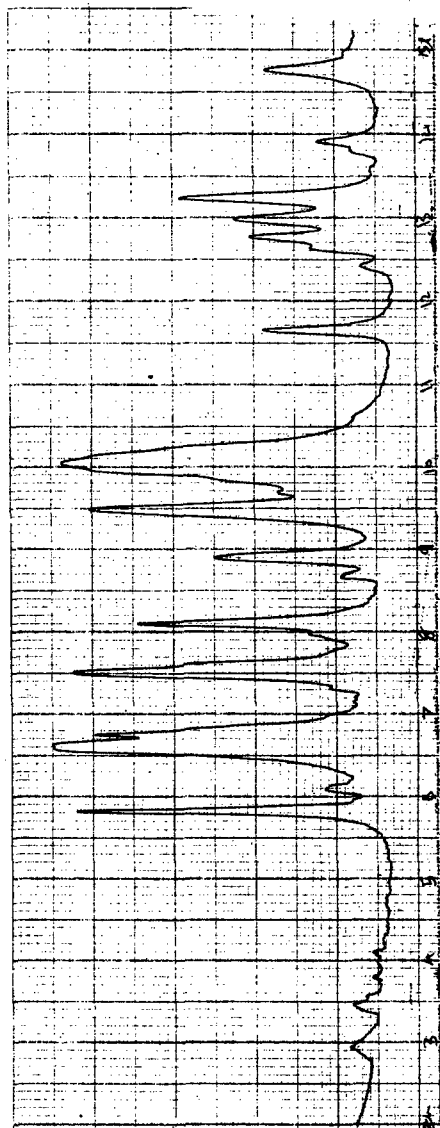
Possibly o-di(tetrafluorophthalimido)tetrafluorobenzene (KCl disc)  
See page 87.



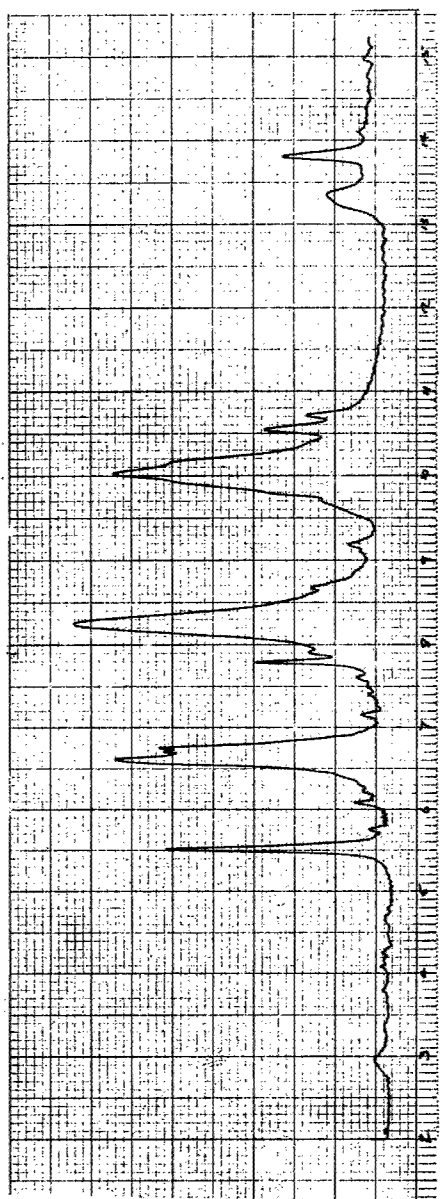
m-Di(tetrafluorophthalimido)tetrafluorobenzene (KCl disc)



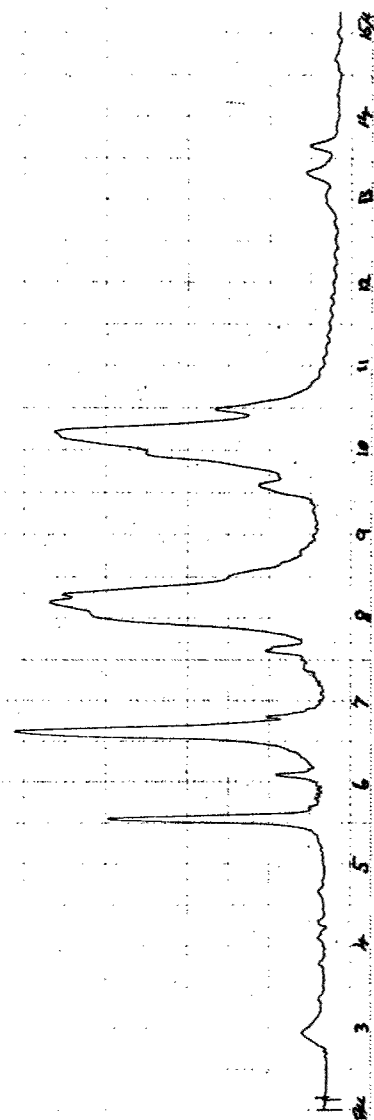
p-Di(pentafluorobenzamido)tetrafluorobenzene (KCl disc)



N,N,N',N'-Tetra(pentafluorophenyl)tetrafluoroterephthalamide  
(KCl disc)

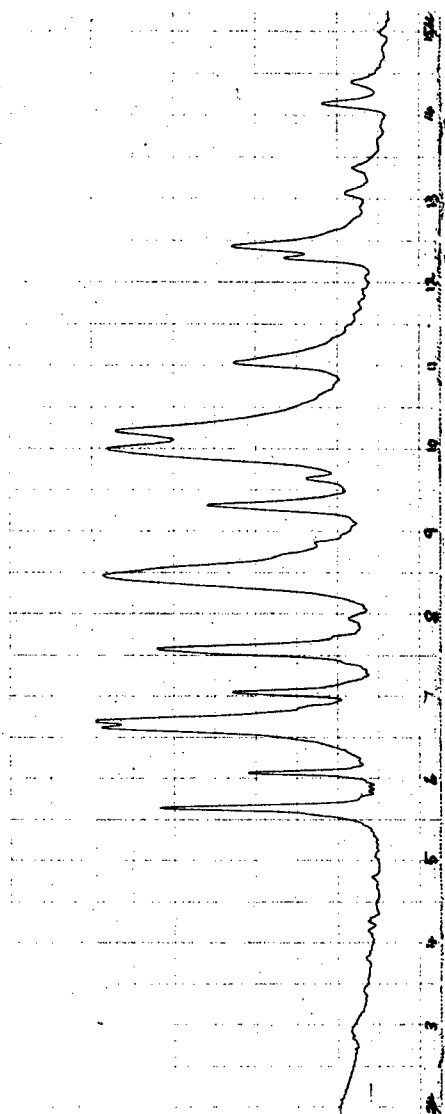


Di(pentafluorophenyl)octafluoro-4,4'-biphenylene biscalbonate (KCl disc)

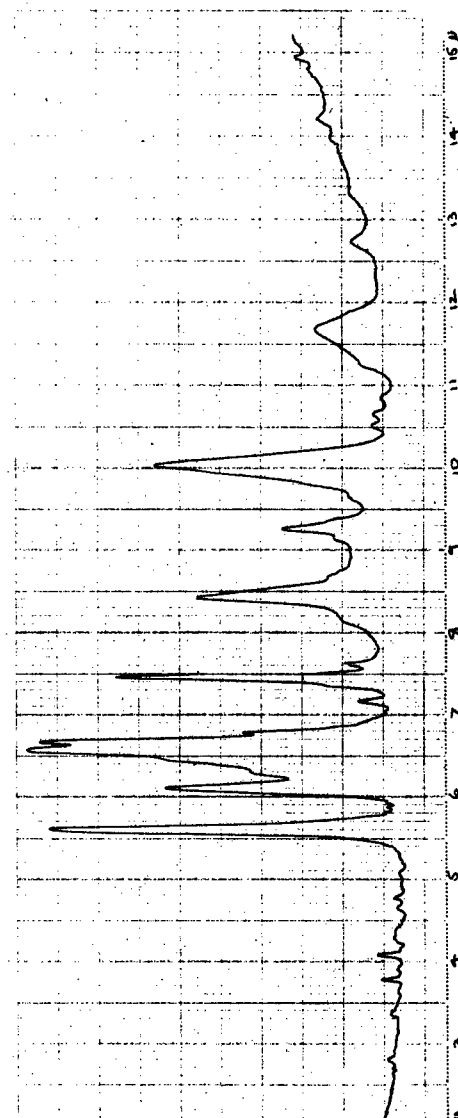


Di(pentafluorophenyl)tetrafluoro-m-phenylene biscalbonate (KCl disc)

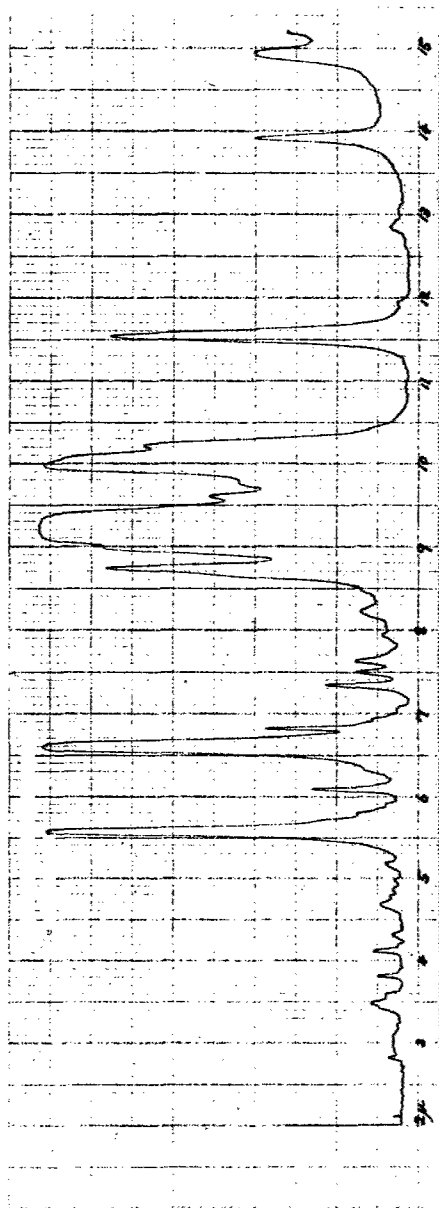




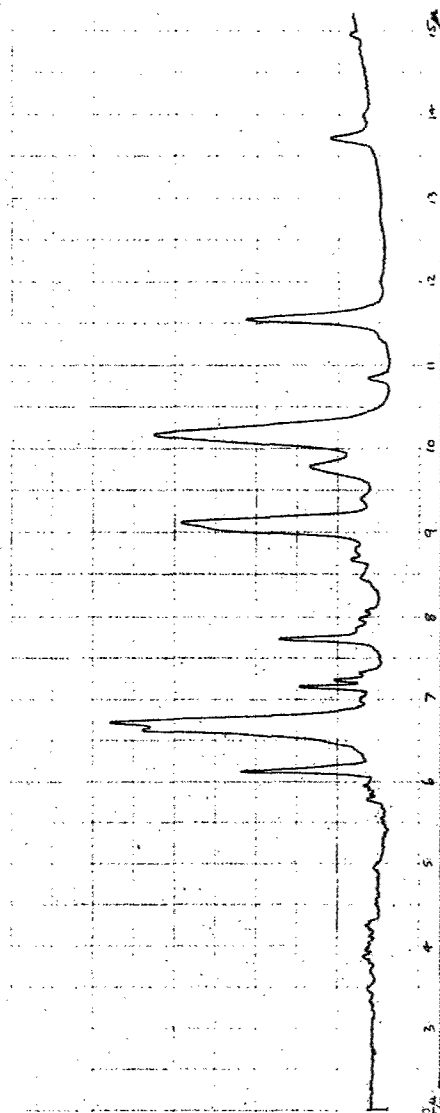
1,3-Di(pentafluorobenzoyloxy)tetrafluorobenzene (KCl disc)



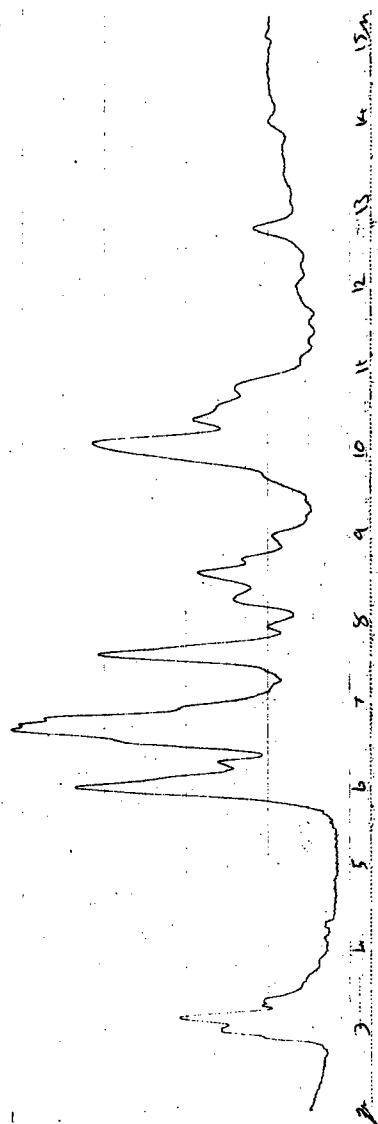
Di(pentafluorophenyl)tetrafluoroisophthalate (solution in  $\text{CCl}_4$ , 2-7.5;  
 $\text{CS}_2$  7.5-15)



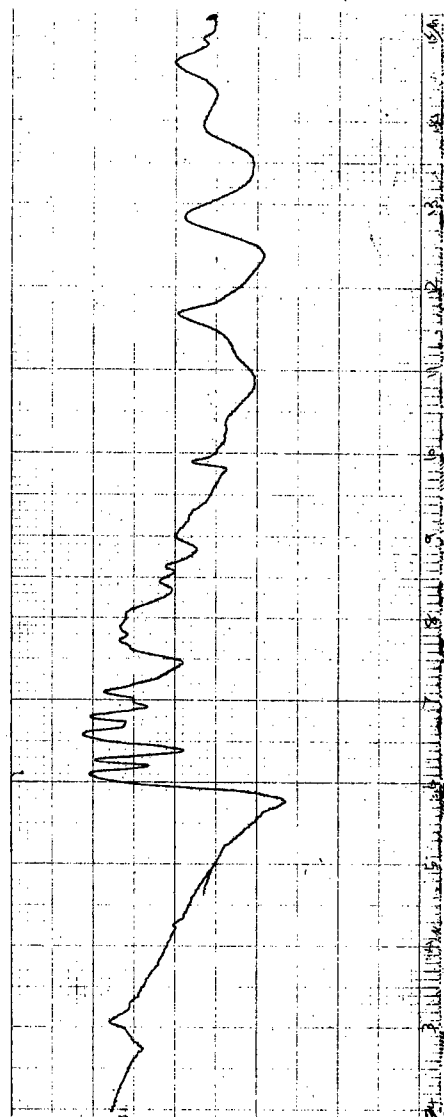
Pentafluorophenyl chloroformate (Film)



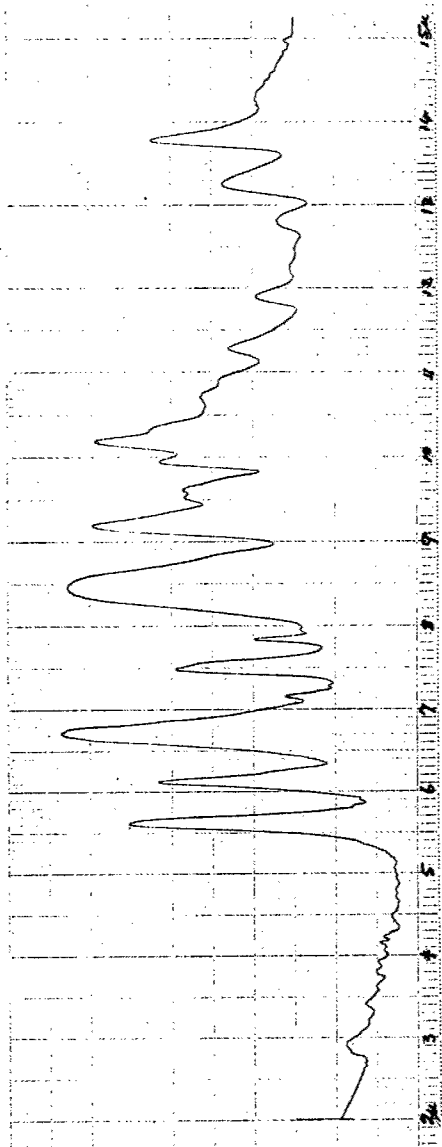
Pentafluorophenylsulphenyl chloride (Film)



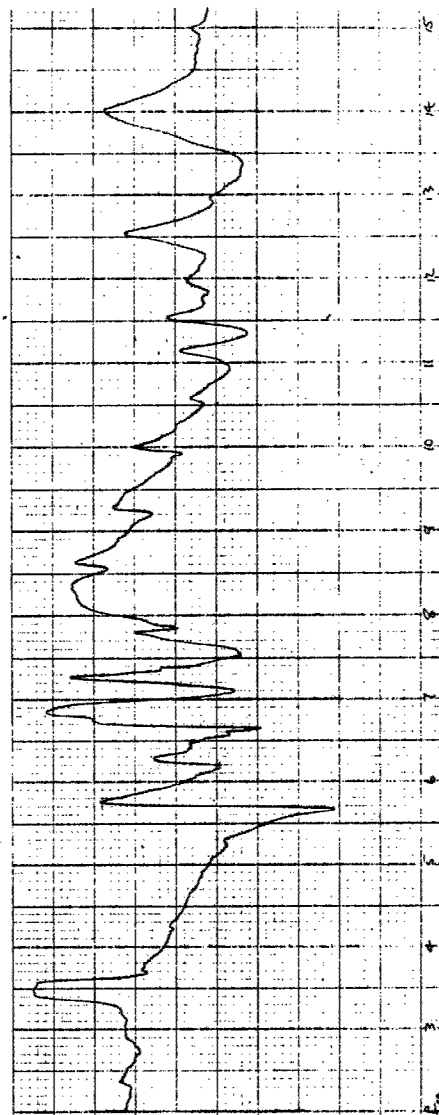
Poly(tetrafluoro-m-phenylenetetrafluoroterephthalamide) (KCl disc)



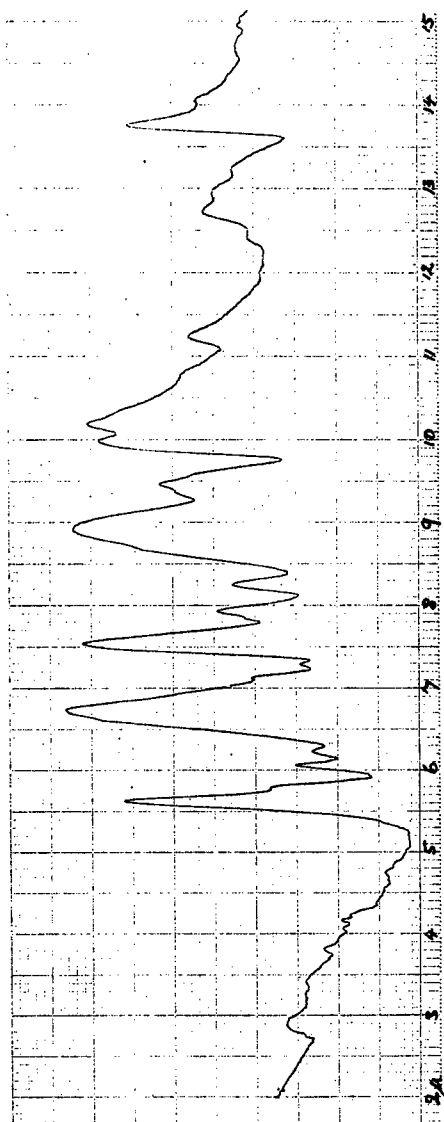
Poly(m-phenylene terephthalamide) (KCl disc)



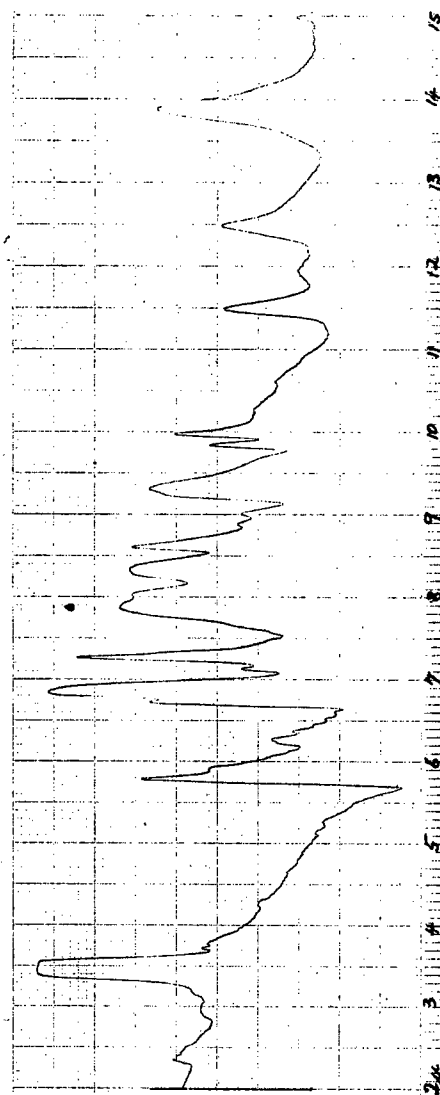
Poly(octafluoro-4,4'-biphenylenetetrafluoroisophthalate (KCl disc)



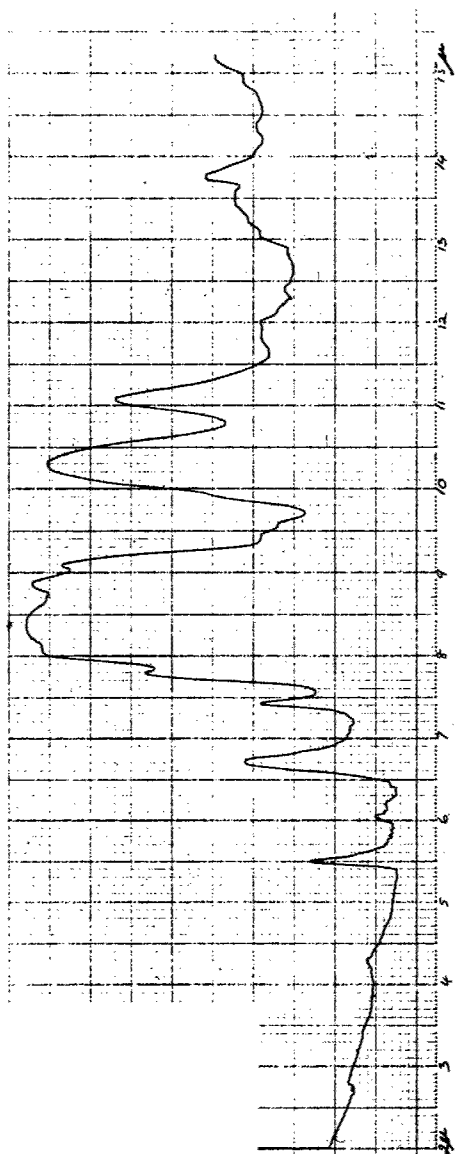
Poly(4,4'-biphenylene isophthalate) (Nujol mull)



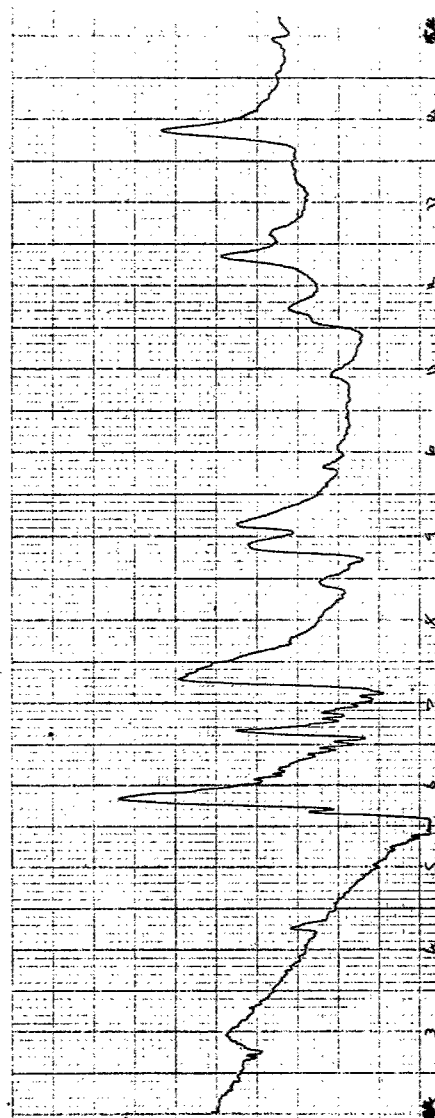
Poly(octafluoro-4,4'-biphenylene tetrafluoroterephthalate) (KCl disc)



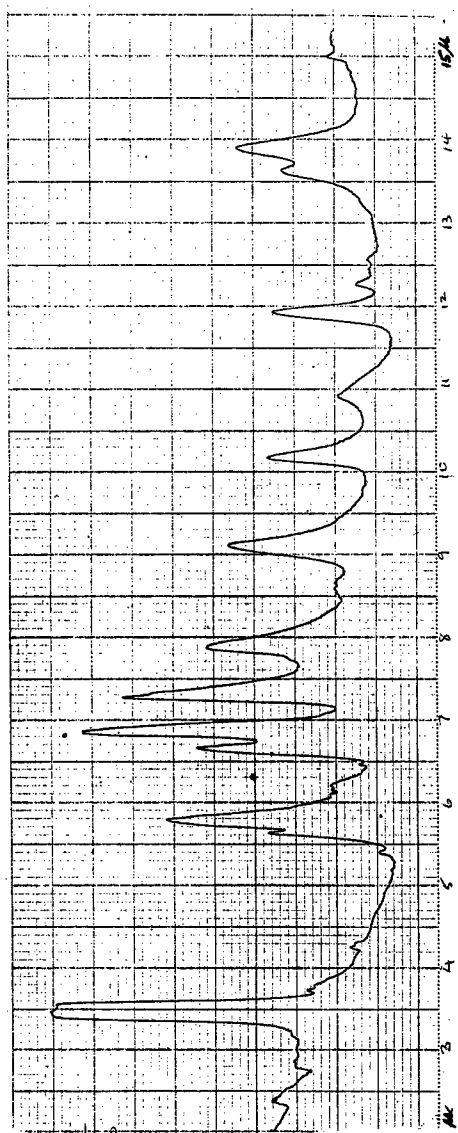
Poly(4,4'-biphenylene terephthalate) (Nujol mull)



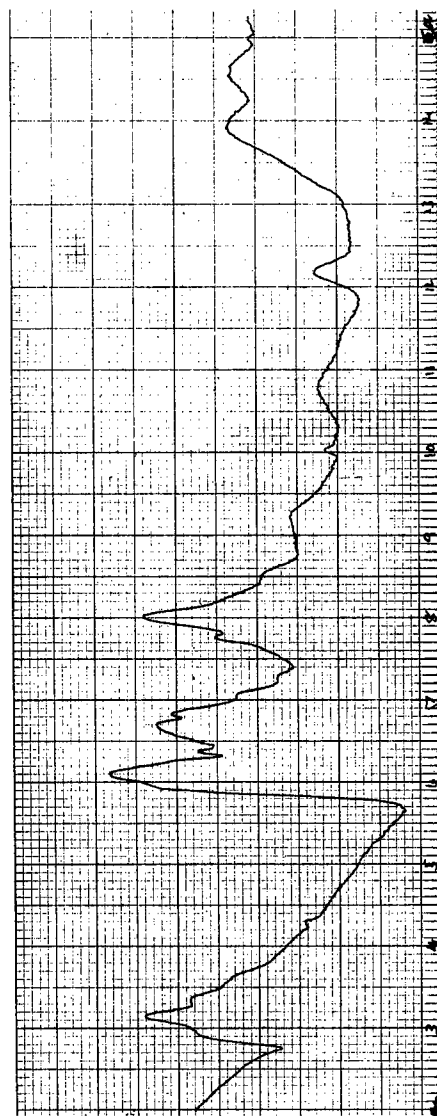
Poly(octafluoro-4,4'-biphenylene carbonate) - preparation (a), page 100.  
(Fluorolube mull)



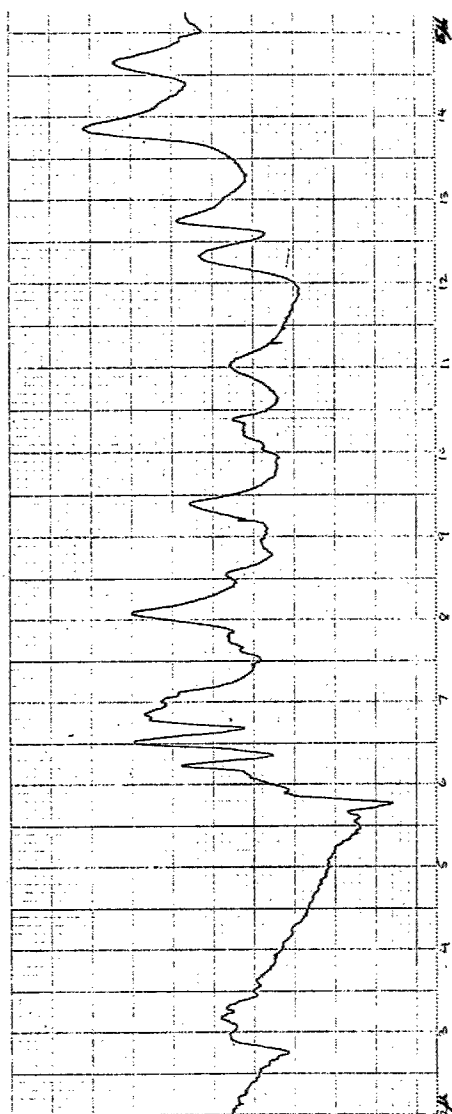
Poly(p-phenylenepyromellitimide) (KCl disc)



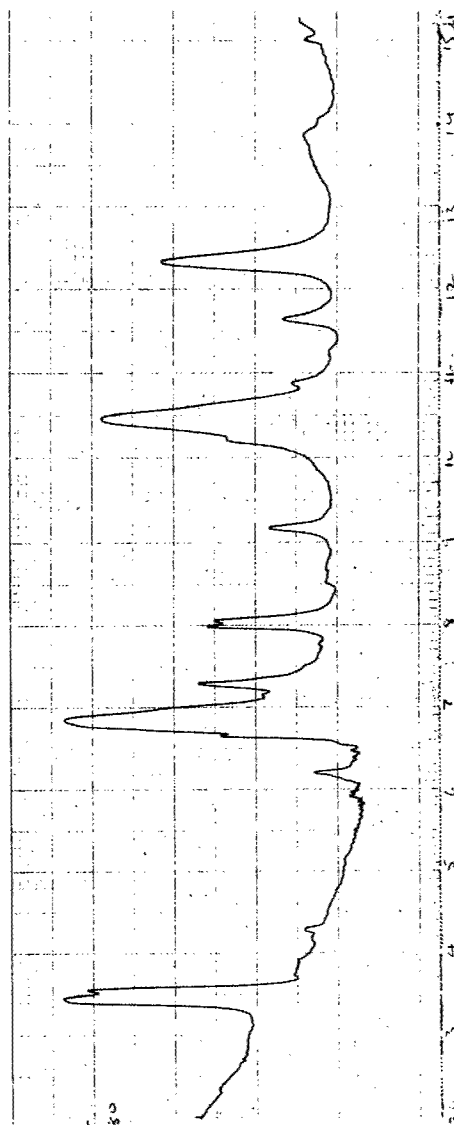
Poly[2,2'-(tetrafluoro-p-phenylene)pyromellitimide] (Nujol mull)



Poly(isophthalhydrazide) - preparation (a), page 105 (KCl disc)



Poly[2-(m-phenylene)-1,3,4-oxadiazolyl-5] (KCl disc) - preparation (a), p. 105



Poly(tetrafluorophenylene sulphide) (Nujol mull)



Unclassified  
Security Classification

DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
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4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report - 1 Dec 1963 - 30 Nov 1964		
5. AUTHOR(S) (Last name, first name, initial) Buxton, M. W.; Tilney-Bassett; and Mobbs, R. H. Cummings, W. and Lynch, E. R.		
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d.		
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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Nonmetallic Materials Division, Air Force Materials Laboratory, Research & Technology Div., Air Force Systems Command, WPAFB, Ohio	
13. ABSTRACT  Preparations or synthetic studies have been carried out on tetrafluoroisophthalic acid, difluoropyromellitic acid, the tetrafluorophenylene diamines, decafluorodiphenylamine, 3,3',-4,4'-tetra substituted-hexafluorobiphenyls, tetrafluororesorcinol, perfluoroaromatic thio-ethers, and dithiols. These and other perfluorinated aromatic compounds are the intermediates employed in the synthesis of perfluorinated model compounds and polymers. The thermal stabilities of such compounds and polymers have been compared with the thermal stabilities of their hydrogenic analogues. Structures investigated include amides, imides, esters, carbonates, oxadiazoles, triazoles and sulphides.		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Perfluoroaromatics Monomers Thermally Stable Polymer Synthesis						

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